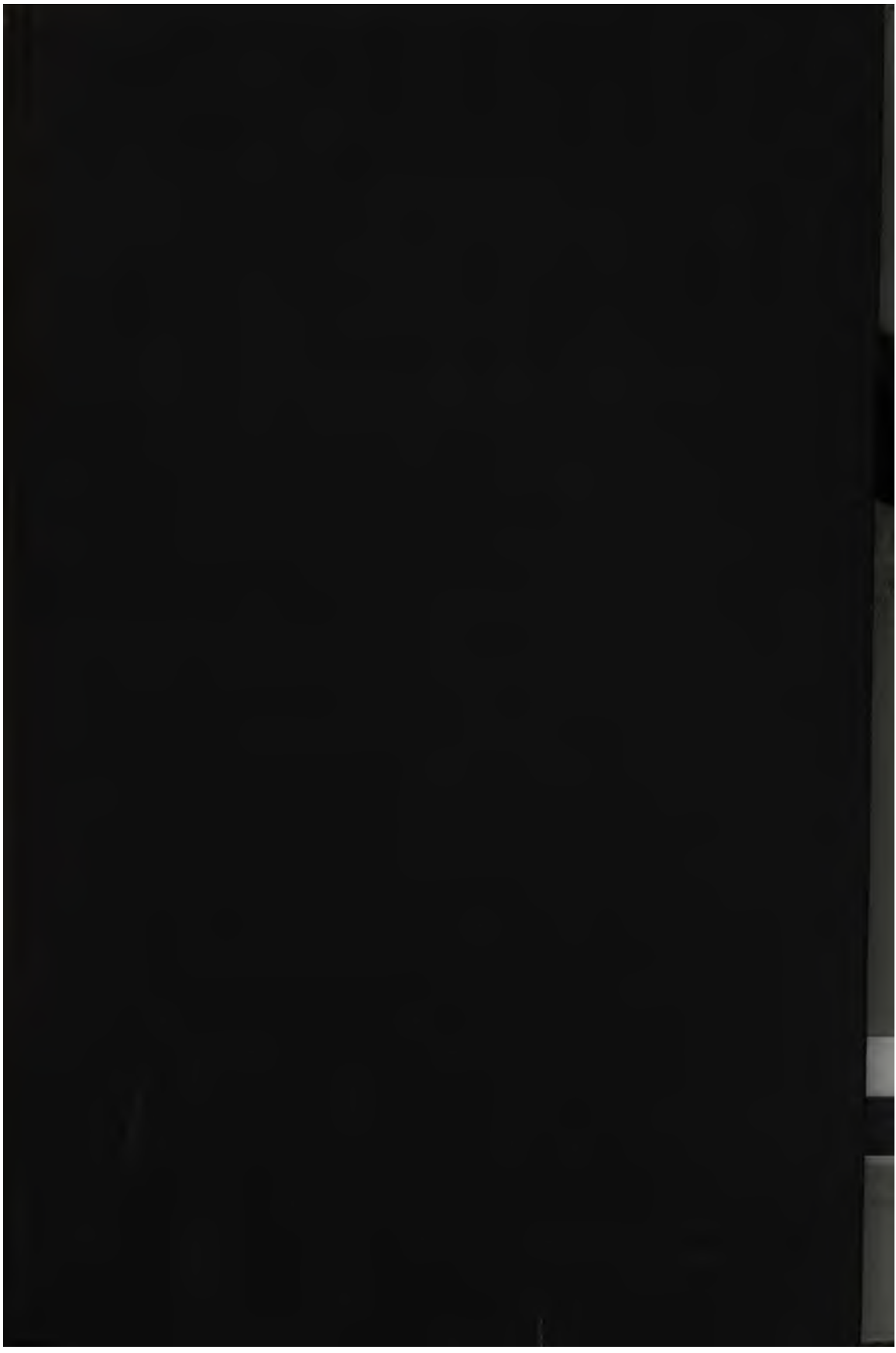


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HISTORY

OF

ANILINE BLACK

BY

E. NŒLTING

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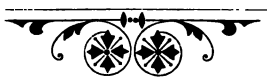

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AUTHOR'S PREFACE.

THE importance of Aniline Black in dyeing and in printing is increasing from day to day, and the number of publications to which the color has given rise is already very considerable.

In many countries the application of Aniline Black is entirely free; in France the patents of Grawitz are claimed to monopolize that industry, and have provoked a great many suits.

It seems to us interesting to compile the most important documents relative to the scientific and industrial history of Aniline Black, and to subject, at the same time, the patents of Grawitz to a thorough discussion.

E. NŒLTING.

ANILINE BLACK.

As the discovery of Aniline Red is due to the observations of Natanson and Hofmann, so the discovery of Aniline Black can probably be traced to the very old researches of Runge, Fritzsche and Hofmann.

Runge[1] in 1834 observed the following facts:

If chloride of copper was added to nitrate of kyanol (aniline), and heated on a porcelain plate to 100°C., a dark green color was produced which changed to black.

A drop of a solution of hydrochloride of kyanol placed on a porcelain plate at 100°C., and treated with bi-chromate of potash produced a very black spot which contained in addition a red coloring matter.

Hydrochloride of kyanol printed on cotton colored with chromate of lead produced in twelve hours green figures which resisted washing.

Fritzsche[2], on the other hand, made the following experiments on aniline derived from indigo:

If chromic acid was added to a salt of aniline, a precipitate was formed which soon become dark green, changing to bluish black, while the chromic acid was precipitated, serving in dilute solutions of aniline as a good reaction for detecting that substance.

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[1] RUNGE, *Moniteur Scientifique* 1863, pp. 533–534.

[2] FRITZSCHE, *Journal für praktische Chemie* XX. 454 (1840).

The precipitate always left on calcination a large amount of oxide of chromium, and it was also formed in an acid solution.

The author[1] vainly attempted to establish the composition of the body in question. According as more or less chromic acid was used, and the solution was more or less strongly acidified, products were obtained differing in external appearance while products identical in appearance yielded different results on analysis. The proportion of carbon varied from 33.93% to 62.66%, and that of oxide of chromium from 31% to 2.12%.

The same chemist[2] on adding a solution of a salt of aniline in an equal volume of alcohol to a solution of chlorate of potash acidified with hydrochloric acid, observed that it formed more slowly but also more certainly a flocculent precipitate of a beautiful indigo-blue color. If the solution was a little more concentrated the mass had a pasty consistency. On filtering and washing with alcohol the blue color changed as the acid disappeared, to a green, leaving on drying a dark green body of considerably less bulk. This contained 16% of chlorine in accordance with the equation:

$$C_{24}H_{20}N_4Cl._2O=4C_6H_7N-8H+O+2Cl.$$[3]

The mother liquors from the blue body gave on subsequent treatment, chlorate of potash and the acid hydrochloride of chloranile.

By the mutual action of chlorate of potash and hydrochloric acid on an easily oxydized body such as alcohol, chloric acid evidently forms other chlorine compounds containing less oxygen than itself. From these

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[1] FRITZSCHE, *Journal für praktische Chemie* XXVIII, 203 (1843).

[2] *Ibid.*, p. 202.

[3] The formula is incorrectly reproduced by KOPP, *Moniteur Scientifique* 1861, p. 75, and also the *Dictionnaire de Wurtz*, Vol. I, p. 325.

considerations Hofmann[1] was doubtless led to study the action of chloric acid or hydrochloride on aniline, and he very readily and instantly obtained the blue body of Fritzsche.

Beissenhirtz[2] on adding aniline or one of its salts to concentrated sulphuric acid and a few drops of bichromate of potash, observed that the mixture produced a pure blue color which almost immediately disappeared.

Crace-Calvert,[3] Clift and Lowe, and also Willm, obtained the blue-green color of Fritzsche by making chlorate of potash to react on hydrochloride of aniline, and had an idea of producing the same color on the fibre, as we shall see further on.

Willm also obtained it by mixing perchloride of iron with nitrate of aniline, the liquid in a short time turning violet and depositing a blue precipitate. The chloride of iron is replacable in this reaction by bichromate of potash.[4]

Emile Kopp[5] repeated the experiments of Fritzsche and made a great number of tests on the action of oxidizing agents on aniline.

On mixing an aqueous solution of nitrate of aniline with powdered chlorate of potash, and subsequently adding a strong acid such as nitric, oxalic, tartaric or hydrochloric acid, with a little sugar to moderate the reaction, no immediate change was observed.

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[1] HOFMANN, *Liebig's Annalen*, XLIII, p. 66, and *Moniteur Scientifique* 1861, p. 75

[2] BEISSENHIRTZ, *Liebig's Annalen* LXXXVII, p. 376.

[3] CRACE-CALVERT, *Lectures on Coal-Tar Colors*: Manchester, Palmer & Howe, Publishers; 1 and 3 Bond street, London, Trübner & Co.

[4] J. Persoz observed the formation of the green color in question instantly on warming a mixture of solutions of perchloride of iron and hydrochloride of aniline. *Treatise on Chemistry, Pelouze and Frémy*, edition of 1860-62, and vol. VI, p. 291.

[5] EMILE KOPP, *Moniteur Scientifique* 1861, p. 75.

The mixture was allowed to stand at a moderate temperature.

In about eight hours a very dark colored precipitate was observed. This precipitate filtered and washed immediately with pure water and then with dilute ammonia, became blue. On drying, it was readily pulverized and possessed intense coloring properties.

On treatment with alcohol, a certain quantity of the coloring matter dissolved with a violet color, the residue, insoluble in alcohol, presenting an intense pure blue color.

The same residue dissolved in cold sulphuric acid, and easily on warming with a blue color, becoming more reddish on heating, and decomposing on boiling.

On repeating the same operations on fabrics, the same very interesting phenomena of coloration were observed as had previously been described by Willm.

The proportions of the constituents may be varied without sensibly altering the result.

For example, 10 parts of aniline were supersaturated with 15 parts commercial nitric acid (forming acid nitrate of aniline) diluted with 6 to 8 times its weight of water.

After thickening with gum or dextrine, 10 parts of sugar and 4 to 8 parts of chlorate of potash (or still better of the more soluble chlorate of soda) were added.

The following proportions may also be employed : 10 parts aniline, 12 parts commercial nitric acid, 50 water, 4 sugar, 2 to 4 chlorate of potash, or of soda, and a sufficient quantity of gum.

On allowing the mixture to cool, it commences to take a bluish or greenish color, indicating the beginning of the reaction. It still remains perfectly transparent.

It is then printed on cotton cloth.

The fabric, exposed to the air, begins to acquire a color, and at the end of 24 or 36 hours, presents the design in a very intense and often beautiful green color.

The color is fixed on the fabric by drying at a moderate temperature.

The proportions of materials and quantity of water may be varied to produce a more or less intense green color and shades varying in purity.

The design remains green on washing the fabric with slightly acidified water.

However, on washing with calcareous or slightly alkaline water. the color changes to a blue, inclined more or less to violet, and sometimes very satisfactory.

The blue designs, on washing with an acid, become green and are restored to their original color on washing with calcareous or alkaline water. These changes may be repeated many times.

The same phenomena were observed in the isolated coloring matter. It is, therefore, evident that the blue and green compounds are one and the same substance, the difference of color depending on the acidity or alkaline reaction of the solution.

The compound in the neutral state is blue, insoluble in water, alcohol, acids and alkalis. The blue color changes immediately to green in contract with a dilute acid, while alkalis and alkaline carbonates reconvert the green color to a blue or even blue-violet.

This aniline blue is an extremely stable color, resisting soaping and the action of light, perfectly. A cloth dyed with this color has been exposed for four weeks to the direct rays of the sun, (in winter), without the shade being sensibly altered. The same blue was developed by printing with iron and alumina mordants. After 48 hours the cloth was boiled, washed, dyed with madder, washed and soaped twice, when the blue designs were found still perfect but with a bluish grey shade.

This aniline blue is, according to the report, comparable to indigo blue, but differs entirely from the latter in the action of reducing agents, which have no effect on it.

A solution of oxide of tin in an excess of caustic alkali, immediately reduces indigo, but has no effect on the aniline blue, unless the solution be extremely concconcentrated and at the same time heated.

In that case the blue passes to violet-blue and then yellowish brown.

The intervention of nitric acid in the production of this coloring matter is not absolutely necessary.

It can be obtained equally well by replacing the nitrate of aniline by the hydrochloride of the same base. According to the proportions, there is always formed at the same time a larger or smaller quantity of violet. For example the following proportions may be used:

10 parts aniline, 50 of commercial hydrochloric acid, 40 to 50 of water, 4 of sugar, and 1½ to 3 of chlorate of potash or soda.

In order to obtain pure shades, it is important that the reaction be allowed to proceed at a moderately elevated temperature. It sometimes requires many days for its completion.

If heated the reaction becomes violent, resinous matters are formed, and the liquors show dull colors, more or less violet, crimson or red.

It is remarked that the green color is formed most readily on the cloth in the solution, but even in acid liquors a deposit of a blue color may be obtained.

Perchloride of iron reacting on nitrate of aniline produces a very similar blue-violet compound.

If a perfectly natural solution of chloride of iron, prepared by the action of dry chlorine on spirals of iron wire, be employed, mixed with a solution of neutral nitrate of aniline, another reaction is immediately observed. The liquor remains perfectly clear and yellow. Gradually it becomes purple and finally deposits a blue-violet precipitate. The mother liquors remain colored and purple.

On impregnating a cotton cloth with the original

solution and exposing it to the air, a very deep and permanent green color is produced.

On washing the fabric after 48 hours in calcareous water, the color changes to a deep violet-blue.

The same effect is produced by steaming the dried cloth and by then washing with calcareous water after steaming. The presence of the oxide of iron on the fabric, tends to deepen the color, the shade of which may be purified by washing with water slightly acidified with hydrochloric acid and then in a large quantity of pure water.

A blue-violet color is thus obtained, which is unaltered by alkalis, but is changed to a greenish shade by acids.

Instead of employing neutral chloride of iron, ordinary perchloride of iron, obtained by dissolving hydrated oxide of iron in hydrochloric acid and oxidizing the ferrous chloride by a mixture of nitric and hydrochloric acids, may be used.

The solution of chloride of iron being ordinarily acid, the aniline on its addition precipitates a little hydrated oxide of iron, which is redissolved by a few drops of nitric acid.

A greenish liquor is thus obtained, which applied to the cloth, produces greenish spots which become darker in proportion as the fabric is exposed to the air.

On washing with calcareous water the greenish shade is transformed into a bluish violet.

On adding neutral chromate of potash to pure and neutral nitrate of aniline, another reaction is observed, the liquid remaining yellow, and deposits yellow spots when dried upon cloth. However, if pure nitric acid be added to render the liquid acid, a reaction occurs and a blue precipitate is deposited. The liquid retains a pale violet color.

The blue precipitate contains also Perkin's violet,

which is extracted by alcohol and characterized by the beautiful blue color it produces with sulphuric acid.

One other reaction follows :

If dry, red Prussiate of potash and dry nitrate of aniline be ground up together, no reaction takes place and the mixture may be kept indefinitely.

On adding water, a green solution is formed but with no immediate precipitate. On allowing it to stand at about 50°—60°c a precipitate having a very beautiful violet-blue shade is gradually formed. The precipitate, collected on a filter and dried, dissolves in alcohol with a very rich red violet color.

The mother liquors of the precipitate are reddish, and on boiling a new precipitate is formed, but of a much less blue shade, vapors of hydrocyanic acid being evolved at the same time. The last liquors retain a pale yellowish red color.

If in place of this procedure, a mixture of gum, red prussiate of potash and nitrate of aniline, or if a mixture of the dry salts thickened with starch be warmed, a green color is obtained which is easily printed on calico.

The design exposed to a slightly moist and warm atmosphere becomes a clear, lively green, varying with the proportions of red prussiate and nitrate of aniline, to more or less bluish green or even violet.

In steaming or even in washing the green color gradually disappears being transformed into a bluish or reddish violet. Acids change the color at once to a bluer shade, and it becomes somewhat paler with alkalis.

It is not impossible that this reaction, which is distinguished from all others by this circumstance, that it takes place not in an acid solution, but with perfectly neutral compounds, may give rise to useful applications.

In conclusion we will cite one other very remarkable reaction, which we have been able to verify perfectly.

It is the production of this aniline blue by peroxide of hydrogen.

By taking 1 part aniline, 10 commercial hydrochloric acid diluted with 100 water, and adding gradually 2 parts of peroxide of barium, the last dissolves without any appearance of a reaction. Gradually the liquid becomes colored, and in about three or four hours forms such an abundant precipitate that the liquid has the appearance of a thick pulp. Then filter and wash with boiling water. The aniline blue thus obtained possesses the same properties as that obtained by the action of chlorate of potash. The mother liquors contain a small quantity of an aniline violet.

We have thus given in full the interesting article of Kopp.

This compound, blue in the free state and green when acted on by acids, has been called by Crace-Calvert, Clift and Lowe, *Emeraldine.*

By treating emeraldine produced on the fibre by hydrochloride of aniline, chlorate of potash and a persalt of iron or other oxidizing agent, with a dilute solution of bi-chromate of potash or chloride of lime, a black is produced. (We shall revert to this reaction again in describing its application to textile fabrics).

No doubt a body identical with the oxidation products of emeraldine is obtained in the preparation of Perkins' violet discovered in 1856.[1]

On mixing in the cold solutions of equal molecules of sulphate of aniline and bichromate of potash, a black powder forms in about 10 or 12 hours, which is filtered washed and dried. Coal-tar naphtha extracts from this a brown color due to the solution of resinous matters, while alcohol separates the violet color. The residue is a black powder insoluble in ordinary solvents.

This powder contains a large quantity of sesquioxide of chromium, but so far as we know it has not been es-

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[1] *English patent*, Aug. 26, 1856.—*French patent* 36140, April 8, 1858.

tablished whether the chromium is combined with the black pigment or only mechanically mixed with it.

Perkin's violet immediately acquired industrial importance, and numerous other processes for its production were patented and described. In all these processes, as in that of Perkin, the quantity of violet produced was small, the principal product of the reaction being the black.

Bolley, Beale and Kirkham, Chas. Lauth and P. Depoully[1] employed a solution of chloride of lime,[2] Greville Williams solutions of equal molecules of permanganate of potash and sulphate of aniline.

Kay heated 50 parts aniline, 40 of 66° sulphuric acid, 1400 water, and 200 black oxide of manganese to 100° C.

Price obtained a violet color by adding to a solution of one molecule aniline and two of sulphuric acid, one molecule of peroxide of lead, and a red by using two molecules of peroxide of lead.

Finally, Dale and Caro boiled one molecule of a salt of aniline (acetate, hydrochloride, sulphate or nitrate), with six molecules of chloride of copper, for about three hours.[3] The black residue, after the extraction of the violet color, was, from 1862, sold to calico-printers for coloring with albumen.

Up to this time the black was obtained as a laboratory reaction, and as a secondary product in the manufacture of Perkin's violet. From the end of 1865 patents and processes appeared for producing the black in a similar manner.

Bobœuf[5] prepared a mixture of solutions of hydrochloride of aniline and bichromate of potash, *subse-*

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[1] *Dictionnaire de Wurtz*, vol. I, p. 311.

[2] The reaction with chloride of lime had already been announced by *Runge* (loc. cit.).

[3] Crace-Calvert, *Lecture on Coal-Tar Colors*, p. 24.

[5] Bobœuf, *French patent* 68,079, July 15, 1865.

quently adding an acid, or adding a solution of one part of aniline in 2 or 3 hydrochloric acid of 20°-22° Be. to a solution of bichromate of potash.[1]

According to the nature of the salt of aniline employed the precipitate varies in color from black to various shades of blue.

Alland[2] took "20 grams commercial aniline, which he "mixed with 100 grams commercial muriatic acid, boiled "four or five minutes, added, gradually, 5 to 6 grams "caustic potash and about 10 grams bichromate of pot-"ash. A few drops of the liquid, poured into a solu-"tion of chloride of lime or chlorinated soda of about "5°, gave immediately a black precipitate, which was "collected on a filter. The black thus obtained is suit-"able for printing."

Alfred Paraf[3] prepared chlorate of aniline by the action of fluosilicate of aniline on chlorate of potash. This solution could be boiled without showing a trace of black, but on adding one or two drops of hydrochloric acid an immediate black precipitate was formed. The black thus obtained does not contain any of the metal.

It has the great advantage of not becoming green in the air.

According to a note in the *Moniteur Scientifique* of 1864, p. 433, the black residue obtained in the preparation of violet by Perkin's bichromate process, was employed with albumen in printing blacks and greys.

Dullo[4] prepared aniline black in powder by treating hydrochloride of aniline with bichromate of potash, or by a mixture of perchloride of iron and chlorate of pot-

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[1] This recalls the reaction of Fritzsche, who employed a salt of aniline and chromic acid.

[2] ALLAND, *French patent* 68230, Aug. 5, 1865.

[3] ALFRED PARAF, *Bulletin de la Societé Industrielle de Mulhouse*, Session of Aug. 30, 1865.

[4] *Wagner's Jahresbericht* 1866, p. 559.

ash, or finally by oxidizing in an acid solution with permanganate of potash.

To fix the black on cotton, the author first mordants the fabric with iron, and then plunges it in a very dilute solution of aniline and a suitable oxide. (The nature of the oxidizing agent is not specified.)

In 1871[1] Heyl Bros. & Co., of Berlin, put on the market an aniline black for printing with albumen. The process for its preparation was kept secret.

Armand Muller,[2] of Zurich, in the same year announced the production of a black similar to that of the brothers Heyl, perhaps even identical with it, which, after two years, was successfully applied to printing on calicoes.

He says to heat a mixture of:

20	grams	Chlorate of Potash,
30	"	Sulphate of Copper,
16	"	Sal Ammoniac,
40	"	Hydrochloride of Aniline, with
500	cc.	Water,

to about 60°, and then remove from the water-bath. In about 2 or 3 minutes the solution puffs up and disengages irritating vapors, having the odor of chloropicrin. If, after a few hours the mass is not entirely black, it is heated again to 60° C. Then allowed it to stand one or two days exposed to the air. Then wash it with water until it contains no more mineral salts, and keep as a 50% paste. The paste dries in vacuo to a heavy and intensely black powder, to which the author assigns the formula, $C^{12}H^{14}N^{2}O^{11}$. (As will be seen later, Nietzki has shown that the formula is not correct.)

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[1] *Wagner's Jahresbericht* 1871, p. 775.

[2] ARMAND MULLER, *Chemisches Centralblatt* 1871 p. 228—*Wagner's Jahresbericht* 1871, pp. 775–776.

Rheinbeck[1] of Elberfeld prepared aniline black in 1872, by allowing equal parts of aniline, hydrochloric acid and chlorate of potash, to react at ordinary temperatures in an aqueous solution, with the addition of a trace of chloride of copper. On allowing the mass contained in a porcelain capsule to dry in the air, again moistening it, and repeating the operation, a black powder with greenish reflex resulted. On examining the washings it was found that all the aniline was transformed, but that they contained the residue of the chlorate of potash and an ammoniacal liquor.

The well-washed powder leaves no residue on incineration. The product was 120.5 % of the weight of aniline employed (the aniline containing toluidine). This black powder is the hydrochloride of a base which in the free state is a very dark violet. Carbonate of soda or ammonia extracted 8.9 % of hydrochloric acid.

This base is very powerful, being capable of removing the acid from salts of aniline.

A sample of cotton, on which had been fixed a very thin film of the dark violet base, was colored green by hydrochloride of aniline even in presence of an excess of aniline.

The greenish aniline black, before treatment with alkali and acted on by sulphuric acid, evolved vapors of hydrochloric acid like other hydrochlorides. It formed a violet solution from which water threw down a greenish black precipitate, doubtless the sulphate of the base.

Rheineck also repeatedly tried the experiment with pure aniline, obtaining in that case a yield of 114.8 %. In both these cases a very small quantity of a soluble organic substance was formed, so the conversion of aniline into aniline black may be considered a very complete reaction. The proportion of nitrogen evolved as

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[1] RHEINECK, *Dingler's polytechnisches Journal* CCIII, p. 485—*Wagner's Jahresbericht* 1872, p. 710.

ammonia was in one experiment one-eighth to one-ninth that of the aniline used, and even less in another experiment.

Rheineck proposes for the base of the black the name *Nigraniline.*

At the session of June 5, 1874, Glanzmann[1] presented to the *Société industrielle de Rouen* five samples of aniline black differing in composition and appearance but agreeing in fastness.

All these blacks were perfectly fast to acids, alkalis and light, they never became green, but sometimes mixed with clear grey. The shades were very solid, varying from grey to lamp-black, without possessing a disagreeable yellowish lustre. In this way it may be well employed without mixing with blue.

The first black was obtained as follows :

Heat to boiling

1 litre water and
100 grams hydrochloride of aniline, and add gradually a solution of

30 grams sulphate of copper in
600 grams water.

Continue heating and add slowly a solution of

52 grams bichromate of potash in
600 grams water.

Continue boiling three hours, add sufficient water and wash by decantation. Collect on a filter and wash again with ammoniacal water.

Drained down to 425 grams the paste contains 319 grams water and 106 grams of the dry black.

This dry black contained 20% organic black and 80 % of the oxides of copper and chromium.

A second experiment was made in which the copper salt was omitted.

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[1] GLANZMANN, *Bulletin de la Société industrielle de Mulhouse*, Session of June 2, 1874, p. 121.

Dissolve by heating to 60°.

1 litre water,
100 grams hydrochloride of aniline,
80 grams bichromate of potash.

And add gradually

100 grams hydrochloric acid of 22° Bé. and
400 grams water.

Heat to boiling for two hours, until the mass thickens and becomes clear. Collect on a filter, wash and drain to 500 grams.

This paste contains:

325 grams water.
175 grams dried black.

The dry black consisting of:

60 % organic black.
40 % oxides of chromium.

In order to oxidize aniline with bichromate of potash, it is not necessary to take a salt as the base oxidizes very readily, and the black contains as large a proportion of oxide of chromium. This does not form simply a mixture, but appears to be combined with the organic matter, thus accounting for its great solidity. On analysis almost constant quantities of oxide of chromium were found. In order to extract this completely, it is necessary to destroy the black, which on treatment with aqua regia leaves a voluminous mass of a brown color which burns without leaving any residue.

Blacks were made by the direct oxidation of aniline in the following proportions:

	No. 3.	No. 4.	No. 5.
Aniline....	100 grams.	100 grams.	100 grams.
Bichromate	100 "	200 "	400 "
Water.....	1000 "	1000 "	2000 "

Heat to boiling for 3 hours. Wash by decantation, drain on filter to 100, 200 and 300 grams respectively of lake.

The three pastes contained 24, 47 and 84 grams of dry material, and the dry black 58, 57 and 53 % of organic black and 42, 43 and 47 % of chromic oxide.

The black was rendered more intense in direct proportion to the bichromate employed. The composition of the products changes slightly, while the proportion of oxide of chromium remains nearly constant.

(Here comes in order of date Grawitz's first patent, 105130 of September 30, 1874.)

In 1875 Coquillion[1] succeeded in forming aniline black by passing a current from two Bunsen elements for 20 to 24 hours, through a concentrated solution of sulphate of aniline. The positive electrode of platinum became in that time covered with a compact black mass, which washed in alcohol and ether, presents the appearance of a black amorphous powder having a green reflex, insoluble in most solvents. This black produces in concentrated sulphuric acid, a green color, and by the action of alkalis becomes an intense velvety black. Hydrogen is evolved in this reaction. The same results were obtained where carbon electrodes were employed.

Nitrate of aniline gives the same result with platinum electrodes, becoming an equally velvety black with alkalis and coloring sulphuric acid maroon with simultaneous decomposition. The hydrochloride of aniline does not give a perfect result. The acetate and tartrate give different products.

In a later work Coquillion[2] confirms the fact that

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[1] COQUILLION, *Comptes Rendus* LXXXI, p. 408. *Wagner's Jahresbericht*, 1875, p. 952.

[2] COQUILLION, *Bulletin de la Société Chimique de Paris* XXV, p. 46 *Wagner's Jahresbericht* 1876, p. 937.

the blacks obtained from the nitrate or acetate of aniline are distinguished from the one obtained by means of the arseniate, phosphate, hydrochloride and sulphate by their action on sulphuric acid.

The black from the arseniate and phosphate dissolves in sulphuric acid with a violet red color, the solution is precipitated on the addition of water in green flocks; the blacks from the hydrochloride and sulphate act in the same manner, but their formation by the current is much more rapid than in the case of the first two salts. The green flocks readily become black on treatment with potash or ammonia.

The electrodes being of carbon must be cleaned with the greatest care. It was therefore demonstrated that the black was formed by nascent oxygen without the intervention of any metal.

The experiments of Goppelsrœder on the formation of aniline black by electrolysis, are even anterior to those of Coquillon, but they were not published until after the first announcement of the latter.[1]

The results obtained by these two investigators, in which they have studied the same question, are mutually confirmative, but Goppelsrœder has included in his researches not only aniline but a great number of other aromatic bases.

By passing a current through a solution of hydrochloride or sulphate of aniline, there is formed immediately on the positive electrode a green deposit, which successfully passes to violet, violet-blue, and intense indigo-blue, almost black. If the current is reversed while the color is violet, it is decolorized and the original negative electrode shows the same series of color changes. The indigo-blue deposit formed on the positive pole, is a mixture of various colors of which aniline black is the principal constituent. On eliminating the bye-pro-

[1] *Etudes électrochimiques des dérivés du benzol*, Mulhouse, 1876.

ducts by boiling with alcohol, a velvety black powder is obtained insoluble in all ordinary solvents, and colored dark green by acids. Fuming sulphuric acid transforms the electrolytic black into a sulpho-conjugated acid, which is insoluble in water but soluble in alkalis.

The analysis of the black obtained directly by Goppelsrœder yielded the formula $C_{24}H_{20}N_4H\ Cl$. The product treated with an alkali yielded the free base of which the simplest formula was C_6H_5N, corresponding exactly with the results of Nietzski and Kayser, which will be alluded to later. Goppelsrœder deduced from the formula of the hydrochloride a molecular weight of $C_{24}H_{20}N_4$ for the base.

Goppelsrœder also described a number of transformations and reactions of aniline black, as also the action of the current on other organic bases. For the details of these experiments, which we are unable to give in full, the reader is referred to the original memoir.

In 1876, Richard Meyer[1] also obtained aniline black by the action of permanganate of potash on very acid solutions of sulphate of aniline. The solutions of the hydrochloride gave identical results, but the author prefers sulphuric acid, on account of the formation of chlorinated derivatives. On mixing the concentrated solutions the author obtained a dark olive precipitate, almost black, the sulphate being black, and changed to blue-black by alkalis. This black is insoluble in ordinary solvents but dissolved in concentrated sulphuric acid with an intense bluish black color. The original body is reprecipitated on the addition of water. The author leaves the question undecided whether his black is identical with that of Coquillon and Goppelsrœder.

In the same year appeared the important researches of Nietzki and Kayser.

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[1] *Berichte* IX, p, 141.

Nietzki[1] analysed the black prepared by the process of Armand Muller.

The crude product was first treated many times with boiling hydrochloric acid, dried, pulverized, and successively extracted with benzine, ether, petroleum ether and alcohol. The author found that the purification could be sufficiently but more slowly effected by alcohol containing hydrochloric acid. The residue was a compact dark green powder. Alkalis transformed it into a very dark violet, which after drying assumed a bronze aspect. The green powder is the hydrochloride of the violet base. Heated alone or with iodide of calcium it gives a distillate containing a large proportion of aniline. The hydrochloride is soluble in aniline, and the base dissolves even more readily in it. Hydrochloric acid reprecipitates the black hydrochloride, a large part however remaining in solution.

The hydrochloride dried at 100°c. gave the following results on analysis :

C	68.29	68.95	69.15	—	—	—	—
H	4.90	5.10	5.26	—	—	—	—
N	—	—	—	13.65	—	—	—
Cl	—	—	—	—	11.64	11.84	11.88

The author deduced from this the formula, $C_{18}H_{15}N_3.HCl$, which requires 69.70 *C*, 5.17 *H*, 13.57 *N*, and 11.47 *Cl*. By treating the black for some hours on a water-bath with fuming sulphuric acid and subsequently pouring into water, a precipitate resembling the original black was obtained, insoluble in dilute sulphuric acid, but soluble in pure water with a dark green color. Its salts are amorphous, the sodium salt is soluble and the barium and silver salts insoluble in water. The body is evidently a sulpho-conjugated acid of the black.

On dissolving the black is concentrated sulphuric acid

[1] *Berichte* IX. p. 616.

and adding a little nitric acid, the violet color passes to a yellowish brown. Water precipitates from this a clear brown body, soluble in alcohol and alkalis with a dark yellow color. Acids reprecipitate the alkaline solution.

Oxidized by sulphuric acid and bichormate aniline black is converted with an excellent yield into quinone.

Goppelsrœder deduces for the hydrochloride of aniline black the formula $C_{24}H_{20}N_4HCl$, and Kayser that of $C_{12}H_{10}N_2HCl$.

In a later paper Nietzki [1] amended his formula for the black. With the acid removed, the black contained carbon, hydrogen and nitrogen in the proportions 6, 5 and 1. It is produced by the elimination of two atoms of hydrogen from the molecule of aniline, and its formula is a polymerization of C_6H_5N.

The differences obtained in the proportion of chlorine show that the hydrochloride is readily decomposed on drying. Nietzki found in the electrolytic black dried at 100°C. 11.6 to 11.8 % chlorine, but on raising the temperature to 110°C., 140°C. and 160°C., the amount was reduced to 9, 4, 8, 3 and 5.5 %.

Kayser treated his salts before analysis with an excess of acid and finally washed with alcohol and ether. The thus yielded 15 to 16 % of chlorine, Nietzki operating in the same manner and drying in vacuo found only 13 to 14 %. He was convinced by a series of experiments that this was the maximum quantity of acid the black would retain. He treated weighed quantities of the base with aqueous and alcoholic hydrochloric acid and determined the excess of acid by titration. The results were 13.8. 13.5, 13.2 and 13.7 %. The hydrochloride of the base $C_{30}H_{25}N_5$ requires 13.4 % which corresponds very well with the quantity found, for which reason it is probably the correct formula for the black.

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[1] *Berichte* XI, pp. 1093 to 1102.

It combined with 23 and 22.9 % of sulphuric acid, the normal sulphate requiring 17.7 % and the acid sulphate 24.4 %.

The platinichloride did not yield a constant percentage, varying between 19 and 22 % of platinum.

On heating aniline black with anhydrous acetic acid, a clear grey powder was obtained which was as insoluble in aniline than in concentrated sulphuric acid. The analysis gave results agreeing well with the formula $C_{30}H_{23}N_5\ (C_2H_3O)_2$. The action of reducing agents on aniline black is particularly interesting.

If the finely divided base is heated with alcoholic potash and zinc dust, it is decolorized, while the leuco-derivative which is as insoluble as the primitive body, regained its color immediately in air.

On boiling with tin and hydrochloric acid or with acid chloride of tin, a bluish green body is obtained, from which the green salt is but slowly reproduced, but which on treatment with alkalis is quickly transformed into the black base.

By the prolonged action of tin and hydrochloric acid or of hydriodic acid of sp. gr. 1.7 and white phosphorous, is obtained, besides resinous matters, paraphenylene-diamine, $C_6H_4\ (NH_2)_2$, and dipara-diamido-diphenylemine, $NH\,(C_6H_4.NH_2)_2$.

On treating the black base or one of its salts with bichromate of potash, a violet-black body is obtained, which does not change to green with dilute acids. The body somewhat resembles the original black, but by burnishing assumes a greenish metallic luster.

This substance appears to be the chromate of the black, as it gives either by calcination or by titration with sulphuric acid 8.17 to 8.33 % of CrO_3. Nietzki considers that this black is not available industrially. We shall see later that this is not correct.

In a later paper Nietzki [1] reported having obtained another aniline black, probably having the formula, $C_{18}H_{16}N_3$, by oxidation of dipara-diamido-diphenylamine, or in larger quantities by oxidizing one molecule of that base with one molecule of aniline; and finally by the oxidation of equal molecules of paraphenylene-diamine and diphenylamine.

By heating the acetate of aniline black for 6 or 8 days with 8 to 10 parts aniline to 150°–160°C., and pouring into water to precipitate the hydrochloride, Nietzki [2] obtained a new base essentially different from the black, as the hydrochloride though insoluble in water is easily soluble in alcohol, from which it crystallizes in small needles having a copper lustre. The alcoholic solution of the hydrochloride is blue, alkalis change it to a beautiful crimson. The ethereal solution of the base has a beautiful magenta color. The base itself is blue, insoluble in water, but soluble in the other ordinary solvents. The alkaline solution of the base, as well as its salts, are decolorized by boiling with zinc dust, the color being immediately restored in the air. The acid solutions are also decolorized by zinc.

Concentrated sulphuric acid dissolves the new body with a blue color, and on heating forms a sulpho-acid. Nitric acid dissolves it without apparent alteration, but on heating decomposes it. The author deduces from analyses of the base and its salts the formula $C_{36}H_{33}N_5$ or $C_{36}H_{31}N_5$. Later analyses have rendered the formula, $C_{36}H_{29}N_5$, more probable. It is derived from a molecule of black and a molecule of aniline with elimination of ammonia. However, it is not probable that it is a phenylated derivative of the black: for its properties as well as its composition it is related to the indulines.

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[1] *Berichte* XVII (1884) p. 226.

[2] " IV, p. 1168, and VI, p. 1096.

Antony Guyard [1] succeeded in forming aniline black by the action of a trace of a vanadium salt on a mixture of hydrochloride of aniline and chlorate of potash or soda. If to a mixture of 100 grams water, 8 of aniline hydrochloride, and 3.5 to 4 of chlorate of potash or soda, 1 cc. of a very dilute solution of chloride of vanadium or vanadate of ammonium be added, the liquid becomes dark in a few minutes, and in 48 hours is converted into a thick pulp of aniline black. One part of chloride of vanadium is sufficient to transform 1,000 parts hydrochloride of aniline into black.

By treating orthotoluidine in the same manner that he oxidized aniline, Nietzki [2] obtained a body analogous to aniline black, but slightly soluble in alcohol, and easily in chloroform and aniline.

The base, which corresponds to the formula C_7H_7N, is violet-blue; the salts are green. Acids precipitate the base from its solution in chloroform.

Kayser [3] has studied, from an analytic point of view, aniline black prepared by four different methods; 20 grams hydrochloride of aniline, 10 of chlorate of potash, 240 cc. of water, and 0.02 grams of vanadate of ammonium yielded a greenish black paste, which was filtered, washed in boiling water, dried and extracted with alcohol, the liquid acquiring a brown color. The filtered liquid contains much free hydrochloric acid. The residue was treated with 2% carbonate of soda, then with water, and finally again with alcohol. He thus obtained a voluminous brownish violet powder, which acquired a metallic lustre by burnishing, leaving ash and without chlorine.

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[1] Antony Guyard (Hugo Tamm), *Bulletin de la Société chimique de Paris* 1876, XXV, p. 58.

[2] *Berichte* XI., p. 1097.

[3] *Wagner's Jahresbericht* 1876, p. 977.

Analyses gave results roughly corresponding to the formula, C_6H_5N.

	Theoretical		Experimental.			
C	79.12	78.80	79.02	78.16	—	—
H	5.49	5.81	5.63	5.8	—	—
N	15.38	—	—	—	15.75	15.3

The black in question has feeble basic properties. It dissolves in sulphuric acid with a violet color, and is reprecipitated by water in green flocks consisting of the sulphate. Creosote, aniline and phenol dissolved it with a dark blue color, which in the case of aniline passed rapidly to a brown. On adding to the solution in creosote or phenol 3 or 4 volumes of alcohol of sp. gr. 0.83, a dark indigo-blue precipitate was obtained The blue solution is decolorized by hydrosulphide of ammonium, and colored green by acids. The salts of the base of this black are decomposed by water and more quickly by alkalis. Kayser found in the hydrochloride and the sulphate quantities of acid corresponding to the formulas, $C_{12}H_{10}N_2,HCl$ and $C_{12}H_{10}N_2,H_2SO_4$.

As we have seen above, Nietzki thought the salts contained but little acid.

Another black, prepared according to the process of Armand Muller, showed identical properties, and gave the following results on analysis:

C	78.80	77.95	—	—
H	5.81	5.77	—	—
N	—	—	15.30	15.26

A third black was obtained by allowing to react at ordinary temperatures 20 grams hydrochloride of aniline, 10 grams chlorate of potash, 400 cc. water, and 60 cc., 32%, hydrochloric acid. The black separated completely in about four days, and had the same properties and the same composition as the preceding. The result of the analysis is appended:

C	78.48	78.23	—	—
H	5.74	5.57	—	—
N	—	—	15.69	15.19

A fourth and last black was obtained by heating to boiling 10 grams ferrocyanide of aniline with 10 grams chlorate of potash and 200cc. water. It evolved vapors of aniline and hydrocyanic acid, and formed a black precipitate which was extracted by water and alcohol. The last solvent extracted a large quantity of a reddish brown substance, and there was obtained as a final product a black mass, soluble for the most part with a brownish black color in creosote. This coloration is changed neither by alkalis *nor by acids*. The ferrocyanide black is easily distinguished by this characteristic from the product of the three other methods which appeared identical with it.

Kayser was unable to obtain concordant analyses of this substance.

Finally, in 1884 Liechti and Suida studied an aniline black obtained by the spontaneous decomposition of chlorate of aniline. This salt was obtained by introducing one molecule of sulphate of aniline into a cold saturated solution of one molecule of chloride of barium and the mixture agitated until the double decomposition was effected. In a short time white prisms 3 to 5 cm. long and from 2 to 3 mm. in thickness separated, remaining about unchanged in the liquid, but becoming black in the air and acquiring a metallic luster, soon exploding with disengagement of aromatic and suffocating vapors. If the still moist crystals were exposed to the air, they became black, and if moistened from time to time to prevent explosion, were finally converted without change of form into aniline black.

We have here, therefore, three very interesting instances of pseudomorphism.

The reactions of the solution of chlorate of aniline

black for two minutes with a 2% solution of free chromic acid, they on the contrary obtained a very black product containing from 10.75 to 11.81 % of oxide of chromium, but no longer in the state of the acid but as the sesquioxide, and which could be completely eliminated by hydrochloric acid.

The product still contained chlorine, but less than the original black, and also oxygen.

The analysis yielded the following results :

C	55.87	
H	6.25	
N	10.48	
Cr	8.09	
Cl	6.15	
O	13.16	(by difference)

Or containing about 9% of chromium calculated as $Cr_2 O_3$.

From the result of this analysis it is evident that the chromic acid oxidizes the black and at the same time expels part of the chlorine. By boiling the black one hour with 2% chromic acid, a much larger proportion, 15.02%, is combined.

By thus treating the black, originally basic and giving green salts with acids, with chromic acid, it becomes acid, combines with metallic oxides, and is no longer turned green by acids.

This peroxidized black only has the property of combining with chromium. A black prepared with hydrochloride of aniline, bichromate of potash and an acid, in the proportions required to form $C_{18} H_{15} N_3 HCl$, only contains after washing 0.16% of $Cr_2 O_3$. A black prepared with free chromic acid in the same proportions contains 2.42% of $Cr_2 O_3$.

By boiling the black for two minutes with a very dilute solution of chloride of lime, and subsequently extracting with dilute hydrochloric acid, then with water

and drying at 105°, Liechti and Suida obtained a body of the following composition :

C	62.68
H	6.16
N	12.65
Cl	8.66
O	9.85

This product therefore also contains oxygen. Like the product peroxidized with chromic acid it is unaltered by acids.

On distilling their black, which they call *emeraldine*, but which is certainly not identical with the body previously described under that name, with zinc dust, Liechti and Suida obtained diphenyl-phenylene-diamine[1],

$$C_6H_4\begin{cases} N\begin{cases} C_6H_5 \\ H \end{cases} \\ N\begin{cases} C_6H_5 \\ H \end{cases} \end{cases}$$

(melting at 140°, its acetyl derivative melting at 170°–172°, and its nitrosamine at 108°–110°), together with dipara-diamido-diphenylamine,

$$NH\begin{cases} C_6H_4NH_2 \\ C_6H_4NH_2 \end{cases}$$

and diphenylamine, and smaller quantities of para-phenylene diamine, aniline and ammonia.

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[1] CALM (*Berichte* XVI, p. 2799), obtained a diphenyl-para-phenylene-diamine from hydroquinone and aniline. Notwithstanding certain differences in melting points, this derivative is probably identical with that of Liechti and Suida.

INDUSTRIAL APPLICATIONS.

We divide this chapter into two sections of very unequal importance.

I.—Application of Blacks in powder.

II.—Formation of Blacks on fabrics.

A. In printing.

B. In dyeing.

I.—APPLICATION OF BLACKS IN POWDER.

In the historical introduction we have several times referred to the application of the black residues from the manufacture of Perkin's violet to the printing of fabrics (compare pages 18 and 19).

At first the black powder was only used as a bye-product, but soon became itself a regular article of manufacture.

After Bobœuf and Alland, Dullo described its preparation in 1866, Heyl Bros. placed it on the market in 1870, Armand Muller described a method for its preparation (p. 19), and Glanzmann (p. 21) prepared blacks by the action of chromate which did not turn green. Finally Kruis obtained blacks by the action of salts, mostly those of the heavy metals, on a mixture of chlorate of potash and hydrochloride of aniline.[1]

[1] *Dingler's polytechnisches Journal* CCIII, p, 483. *Moniteur Scientifique* 1874, p. 927.

II.—FORMATION OF BLACKS ON FABRICS.

A. Processes more particularly relating to printing.

The first idea of forming it by the oxidation of aniline on fabrics is, as we have already seen, due to Runge. Willm also made some experiments of this character.[1] At the same time three English chemists, Calvert, Clift and Lowe, attempted to make this reaction industrial.[2]

The following are Crace-Calvert's remarks on the subject in his *Lectures on Coal Tar Colors* (published in 1863), p. 63:

"Although it has been known for a long time to chemists that aniline yielded a green coloring matter when subjected to the action of oxiding agents, all attempts up to the present time to fix the color on silk and wool have failed; but in 1860, Calvert, Clift and Lowe introduced a simple and practical method of producing it, under the name of *emeraldine*, on cotton fabrics. The samples thus printed were exhibited in the chemical section at the Exhibition of 1862.

"The process consists in printing with hydrochloride of aniline on cotton prepared with chlorate of potash; a brilliant green color is in a few hours gradually developed, which only requires washing. If the green fabric is then passed through a solution of bichromate of potash the color is transformed to a dark indigo blue, called *azurine*.

"The direct production of this color on fabrics is very important, and it will probably lead to the production of other colors from coal tar directly on the fibre without previous treatment. In this way not only the

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[1] *Bulletin de la Société Chimique de Paris* 1860, p. 204. (Session of July 27.)

[2] *English Patent*, June 11, 1860. *French Patent*, Dec. 12, 1860.

loss of a great quantity of aniline in the preparation of the color is avoided, but a considerable saving of mordants is also realized.

"The gentlemen also contracted at the end of 1860, with Wood and Wright, to produce greens and dark blues, which were considered sufficiently good to be placed on the market; and Wood and Wright have subsequently made an improvement in the dark shades, which are known as *blacks*, by adding to the chlorate of potash *persalts of iron*, or other oxidizing agents; *and also in oxidizing the color thus produced on the fabric (which is the principal novelty in the process) by a dilute solution of bichromate of potash or chloride of lime.* Nitrate of copper may be mixed with hydrochloride of aniline, without the addition of chlorate of potash, and the mixture printed on fabrics, a green or dark blue being gradually developed. This method of printing on fabrics gives greens or dark blues so dark as to be almost identical with blacks."

In Crace-Calvert's works is a sample of emeraldine which is a dark grey, and a sample printed by Wood and Wright which is a true black.

In 1863, J. Lightfoot, of Accrington, introduced such improvements in the manufacture of aniline blacks that he is generally considered the first introducer.

The color of Calvert, Clift and Lowe, containing very acid hydrochloride of aniline attacked the copper rollers very strongly, and the color thus developed much

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[1] Compare on this subject E. KOPP *Moniteur Scientifique* 1861, p. 219. In that article Kopp repeats the following remark of the editor of the *Chemical News*:

If cloth printed with a salt of aniline is passed through a solution of chromate or bichromate of potash, it is immediately colored a dirty green, and the color changes to a violet shade on subsequent boiling with soap and water.

If the solution of aniline is concentrated the cloth immediately becomes black in the chromate bath.

faster than when printed from wooden blocks. It is from this observation that Lightfoot was evidently led to introduce copper in the same color.

He thus describes his process[1] :

"I take a litre of water in which I dissolve 25 grams of chlorate of potash ; I add afterwards aniline or an analagous derivative, preferably 50 grams of aniline, together with an equal weight of hydrochloric acid. After having agitated these ingredients well, I add to each litre 126 grams acetic acid, 50 grams perchloride of copper of sp. gr. 1.44, and 25 grams sal ammoniac, or an equal quantity of another alkaline chloride ; I immerse the fabric or the yarn in this solution ; wring and dry it ; allow it to stand two nights and pass it through a solution of alkali or soap, or preferably through dilute chloride of lime. By this process I obtain an intense black."

For printing it is sufficient to replace the litre of water by an equal quantity of starch paste. The lustre of the black, its solidity, and its ready sale, sufficiently explain the importance of Lightfoot's discovery, and the eagerness with which every one sought to apply it. Unfortunately this process in its original form presented great inconveniences ; and it was immediately modified, not only by the inventor himself, who indicated certain other metals which could replace the copper used in its preparation, but by all the colorists interested in perfecting it.

At first the chloride of copper contained in the color strongly attacked the steel doctors, occasioning what was termed in the workshop "reducing the doctors," the acid attacking the rollers ; on the other hand the color altered rapidly at ordinary temperatures, owing to the oxidation of the aniline being affected in part before printing, this diminishing and retarding the amount of the

[1] *French Patent* 57192, Jan. 28, 1863.

black formed ; finally the fabrics were much weakened by the acids and acid salts.

Kopp[1] attempted to obviate the inconveniences as follows: "To begin with, the cloth is treated with a weak solution of chlorate of potash, containing according to the description 2 to 4 grams of the salt per litre of water, adding at the same time a certain quantity of arsenite of soda (the quantity of arsenite of soda in the solution is ordinarily a little greater than that of the chlorate of potash). When dry it is printed with the thickened aniline color, containing about 70 grams of dry hydrochloride of aniline per litre, and half that quantity of chlorate of potash and protochloride of iron.

"Operating in this manner the employment of copper salts is dispensed with.

"The protochloride of iron passes by oxidation into the state of perchloride of iron, which, however, possesses an acid character and is capable of acting on salts of aniline, evidently playing the part of the sulphate of copper in the other method of preparation.

"The cloths printed in this manner pass through the same operations and require the same precautions; they are a little less easily attacked, and some kinds, as for example the violet-black, seem to form more readily."

Camille Kœchlin, on the other hand, modified Lightfoot's process, by first working the fabric in sulphate of copper, and then printing with a mixture of chlorate of potash and hydrochloride of aniline.[2]

This process is expensive and much restricts the number of colors which may be combined with aniline black.

In an article signed C in the *Moniteur Scientifique* for 1864, p. 433, the author announces the preparation

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[1] *Moniteur Scientifique*, 1863, p. 531.

[2] *Dictionnaire de Wurtz*, vol. I, p. 326.

of the fabrics with bichromate instead of copper salts to be equally applicable.

Cordillot[1] proposed to substitute for the copper salt of Lightfoot's process, ferricyanides, more particularly ferricyanide of ammonium, in admixture with chlorate of potash, tartaric acid and hydrochloride of aniline.[2]

Cordillot's process, although in some respects superior to the preceeding, has, however, some defects, the expense and instability of the compound at the temperature of the oxidizing room (40°, 50°, C.) However, it has great advantages; the black is beautiful, extremely fast, and *does not turn green on steaming*. For a steam black the hydrochloride of aniline is replaced by the tartrate, followed by the ferrocyanide of potassium, which is less expensive than the ammonium salt, and finally, in fixing, a quantity of chlorate (chlorate of soda or baryta is preferable) equal to that of ferrocyanide. With these slight modifications, Cordillot's process is still used on an extensive scale for steam blacks.

The most important improvement on Lightfoot's process for aniline blacks is that of Chas. Lauth,[3] which process is also in use at the present time, conjointly with the vanadium process of which we will speak later.

Lauth, having proved by many experiments, that the presence of copper or another easily reduced metal[4] is indispensible to the formation of black, and that practice had demonstrated the impossibility of satisfactorily employing metallic salts and particularly those

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[1] *French patent*, 60896, Dec. 2, 1863.

[2] Compare *Moniteur Scientifique* 1863, p. 434, and SCHUTZENBERGER *Traité des matières colorantes*, vol. I, p. 513.

[3] *Bulletin de le Société Chimique de Paris*, II., p. 416 (1864).

[4] Or in accordance with the actual theory of the formation of the black, we should say "of a metal the chlorate of which decomposes easily."

of copper, had resource to the intervention of an insoluble copper compound, inactive at the moment of printing, but subsequently becoming soluble and active. The sulphide of copper employed is transformed in the oxidizing room by the chlorate into sulphate, and the requirements of Lightfoot's process are thus satisfied.

The recipe of Lauth is as follows: 10 litres starch paste, 350 grams chlorate of potash, 300 grams sulphide of copper in paste, 300 grams of sal-ammoniac, and 800 grams hydrochloride of aniline. The fabrics printed with this mixture are taken to the oxidizing room and washed with pure or alkaline water, when the black is developed.[1]

Lauth's process admits of Lightfoot's discovery being employed industrially on a vast scale.

Finally Camille Kœchlin completed the construction of this edifice so painfully raised, replacing the hydrochloride of aniline by the tartrate, a salt absolutely uninjurious, to the most delicate fabrics, and which has the great advantage over the hydrochloride, that it does not attack the mordants immediately adjoining the impression. The tartrate would by itself be incapable of producing the black, but in presence of the sal-ammoniac, of which the proportion is considerably increased, a double decomposition takes place and the hydrochloride is formed on the fibre. It is found at this stage in the ordinary conditions of Lauth's process.[2]

In place of the expensive tartrate, Kœchlin[3] also recommends the employment of a *basic* salt of aniline obtained by adding to aniline saturated with hydrochloric acid an equal quantity of free aniline. The color develops more rapidly in proportion to the acid con-

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[1] *Dictionnaire de Wurtz*, vol. I., p. 325.

[2] *Dictionnaire de Wurtz*, loc. cit.

[3] *Moniteur Scientifique* 1865, p. 773.

tained in the aniline salt, but then the fabric is injured; with too basic preparations of aniline, it is not formed at all, and in practice it is necessary to seek for a medium point.

Alfred Paraf[1] proposes to print blacks by dissolving hydrochloride of aniline in hydrofluosilicic acid, thickening, printing on fabrics prepared with chlorate and potash, and developed in the oxidizing room at 32°–35°C.

Chlorate of potash may also be added to the color if injury to the blankets is not feared.

The pure chlorate of aniline, free from acid, does not give a black at the temperature of the oxidizing room, but forms it in presence of a trace of a copper salt. (Rosenstiehl.) We shall revert to this again on discussing the theory of the formation of aniline-black.

Higgin[2] recommends depositing an insoluble chromate in the fibre, thus obtaining in dyeing or printing a black which is fixed with greater fastness in the fabric. For instance, chromate of copper may be thus fixed by the double decomposition of a neutral chromate and a salt of copper, or the chromate of copper may be dissolved in ammonia, working the cloth in this solution and volatilizing the ammonia by drying at a certain temperature.

If a fabric thus prepared is printed with a thickened solution of an aniline salt, the color appears in patterns, furnishing various shades of grey and black. On these passing the fabric through water containing ammonia, the chromate of copper is redissolved from the unprinted portions, leaving a white ground. Oxide of chromium mixed with an alkaline chlorate and an easy reducible oxide, such as the oxides of iron or copper, may be employed, but only in the condition of arseniates.

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[1] *Société Industrielle de Mulhouse* (Session of Aug, 30, 1865).

[2] *French patent* 73054, Sept. 26, 1866.

According to a supplementary patent of Oct. 25, 1866, Higgin also reserves the employment of tungstate of chromium mixed with chlorate and a salt of aniline.

Alfred Paraf[1] obtains aniline blacks by printing a color thickened with starch, containing 340 grams of the hydrochloride or another salt of aniline, 500 grams chromate of chromium in paste, and chlorate of potash, developing in the oxidizing room. This black stands steaming.

In certain cases, in order to hasten the oxidation, it is advantageous to add to the color 2 to 3 % of hydrofluosilicic or arsenic acid. To prevent the decomposition of the color by the chromic acid which is very easily liberated, a little of a substance which forms an innocuous compound with chromic acid, chloride of barium for example, is added The author, while particularly specifying chromate of chromium, claims in general the employment of chromic acid *in a single operation* as an oxidizing agent (in opposition to the generally used ultimate chromic oxidation), by the employment of insoluble or partially soluble chromic salts, capable of liberating chromic acid when submitted to steaming, such as, for example, *chromate of sesquioxide of iron*, subchromate of lead, or the more soluble salts of chromium and manganese, chromate of manganese, &c.

In Higgin's second French patent, 84,185, Jan. 27, 1867,[2] he proposes to prepare it by introducing into the color, together with chlorate of potash and a salt of copper, a chloride of aniline not containing an excess of acid. To this end he mixes aniline with a solution of a metallic chloride, the base of which does not hinder the formation of black.

By adopting convenient proportion, the precipitation of the metallic base is *in a great part* or altogether

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[1] *French patent*, 71692, May 24, 1866

[2] *Wagner's Jahresbericht* 1869, p. 583.

avoided, by which is obtained a chloride containing the chlorine in combination with a *metal-aniline*. He particularly recommends the sesquioxides of iron and chromium. The observations of Higgins are correct, but the interpretation which he gives is not ; for if the chlorides of iron or chromium are added to aniline, they do not form chlorides of *metal-anilines* or *métal-aniles*, as Schiff called these bodies in 1864, but simply hydrochloride of aniline and a *basic chloride* of iron or chromium, soluble in presence of a little aniline, but precipitated on adding an excess of aniline as the hydroxides of iron or chromium.

In the same patent Higgins reserves the replacement of the sulphide of copper by the sulphocyanide.

This derivative has been, and is still employed in England under the name of white paste.

Spirk[1] recommends printing aniline black with a color composed of 30 grams acetate of copper, 30 grams chlorate of potash, 15 grams ammonia, and 1 litre starch, adding after cooling 75 grams nitrate or hydrochloride of aniline. The color is developed in 8 to 12 hours, and becomes a black on passing through an alkali.

The author afterwards describes other process for printing from rollers a base of sulphate of copper and oxalate or tartrate of aniline, and then a black with tungstate of chromium, obtained by double decomposition of chloride of chromium and tungstate of soda, 2 litres water, 270 grams white starch, and 375 grams tungstate of chromium, are boiled together ; on allowing to cool until lukewarm, add 60 grams chlorate of potash, 30 grams sal ammoniac, and 210 grams hydrochloride of aniline.

French patent 85554, May 5, 1869, of Lauth, is par-

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[1] *Dingler's Polytechnisches Journal* CLXXXIX, p. 255.—*Wagner's Jahresbericht* 1867, p. 673.

ticularly important for dyeing and fixing the black developed naturally in any manner, but he also describes a method for printing, consisting of printing with a neutral salt of aniline, regenerated or precipitated black oxide of manganese, and sal ammoniac or another agent capable of decomposing black oxide of manganese on steaming. The oxide of manganese may be replaced by *other oxides or metallic acids rich in oxygen.*

Experience having demonstrated to colorists that the pure chlorate of aniline, printed entirely in the absence of any metal, from wooden blocks for example, would not develop a black at the temperature of the oxidizing room, but that it readily developed in presence of traces of copper, Lightfoot[1] tried certain other metals possessing analagous properties. He printed from blocks a color composed of basic hydrochloride of aniline and chlorate of ammonia, thickened with starch, and treated the fabric with the metal for five minutes. The fabric was then exposed in a hot and moist place for twelve hours, and then passed through an alkaline bath. The greatest development of color was manifested by *vanadium*, next came *copper*, then *uranium*, then *iron*, the other metals producing but little color.

He was then induced to experiment in replacing salts of copper by the salts of vanadium, which were industrially available, of which, as we shall see, a number can be well employed.

Kruis[2] studied the action of different salts of the heavy metals on cold and hot solutions of chlorate of aniline, and stated that they all reacted more or less rapidly, giving dark green precipitate, which in the air became grey or black. Printed on fabrics with chlorate of aniline, however, few of them produce patterns, ex-

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[1] *Bulletin de la Société industrielle de Mulhouse* 1871, p. 285.

[2] *Dingler's polytechnische Journal* CCIII, p. 483.—*Moniteur Scientifique* 1874, p. 927.

cept copper, vanadium (which the author did not try), iron, manganese and cerium.

The most beautiful black is formed by cerium, it surpasses in intensity, fire and purity that obtained by salts of copper, the manganese black equals that from copper, while that of iron is inferior.

The first patents of Grawitz appeared in September and October of 1874.

In 1874, Wehrlin, Ernest Schlumberger and Brandt published in the *Bulletin de la Société industrielle de Mulhouse* interesting notes on Cordillot's black. Schlumberger gave the prefereuce to colors from ferrocyanides, which had the advantage of keeping well and not attacking the doctors, and Brandt remarks that the black of Cordillot, though not developing well on exposure, furnishes, if suitably modified, *an excellent steam-black*.

The steamed ferrocyanide black, as is known, does not turn green.

Guyard[1] and Witz[2] communicated some very interesting studies on the employment of vanadium for the preparation of aniline black in powder, in dyeing and in printing. Guyard has shown that less than one part of vanadium is sufficient to easily convert 1000 parts of hydrochloride of aniline into black in presence of the necessary quantity of chlorate of potash. Witz has found that vanadium has this property in a remarkable degree, that $\frac{1}{135000}$ or even $\frac{1}{270000}$ is sufficient to obtain a printing in a few days by oxidation at 25°C. Practically he employed in printing a proportion corresponding to 0.0012 grams vanadium per litre of color, containing about 80 grams hydrochloride of aniline, or $\frac{1}{61700}$ the weight of that salt. The quantity of vanadium

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[1] Antony Guyard (Hugo Tamm), *Bulletin de la Société chimique de Paris* XXV, 1876, p. 58.

[2] *Bulletin de la Société industrielle de Rouen* 1876, pp. 310–334.

to be added to the color for black varies generally in inverse ratio to the proportion of aniline, to the surrounding temperature, and to the time allowed to oxidation.

The hydrochloride of aniline is rendered very slightly basic by the addition of 0.5 to 1 cc. of aniline, or an equal quantity of 22° ammonia per litre of color. The proportion of the hydrochloride of aniline to the chlorate of potash is 1 to 0.417, Lauth having recommended a nearly identical proportion, 0.437.

Storck and Strobel[1] observed that sulphocyanides are transformed by the oxides of chlorine into persulphocyanogen. As these oxides also convert aniline into black sulphocyanides (50 grams per litre of gum-water) preserve the black perfectly. In this manner all shades of black may be kept by incorporating with the colors in albumen or tannin 50 to 60 grams of a sulphocyanide. The same good effect is produced on acid colors by sulphocyanide of lead.

D'Andan and Wegelin[2] attempted to obtain blacks which did not turn green by employing a mixture of aniline with xylidine, cumidine or tolindine.[3]

Schmidlin[4] prepared an aniline black for printing, composed of an aniline salt, chlorate of potash, an insoluble chromate, and a per-salt of iron.[5]

A printing color giving good results was composed of by the same chemists of 40 litres starch-paste (containing 1 kilo. starch to 5 litres water), 6 kilos. chromate of lead, 6 kilos. sal ammoniac, 6 kilos. hydrochloride of aniline, and 1.5 kilo. chlorate of soda. Print, steam and wash.[6]

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[1] *Wagner's Jahresbericht* 1879, p. 1090,

[2] *English patent* 1879, 4123.

[3] *Wagner's Jahresbericht* 1880, p, 785.

[4] *English patent* 1879, 3101.

[5] *Wagner's Jahresbericht* 1880, p. 785.

[6] *German patent*, 13428.—*Wagner's Jahresbericht* (1881) p. 875.

Glenck[1] remarked that the chlorates of barium and sodium, and even a solution of chloric acid, were employed on a large scale in printing, insteadof chlorate of potash, which is too slightly soluble. Chlorate of baryta is especially employed in colors with prussiate of potash, but is not put in colors containing sulphates, as the sulphate of baryta renders the shades paler.

Goppelsrœder[2] produced an aniline black directly on the fabric by electrolysis.

According to H. Schmid[3] aniline blacks were being developed by Mather and Platt by oxidizing during one minute at a temperature of 90°c. Schmidlin's black, which is slightly acid, works very readily to this kind of oxidation. Other blacks developing equally well in this manner are composed of chlorate of ammonia or chlorate of aniline and a copper salt, or of an aniline salt, an alkaline chlorate, and ferro—or ferricyanides.

To preserve aniline black hyposulphite of soda may be employed (400 grams per litre), or, according to Horace Koechlin, pyrogallic acid (15 to 20 grams per litre), or, according to Witz, ferrocyanide of potassium (100 to 120 grams per litre), albumen, cashew-nut, acetate of soda, chalk, zinc dust, and according to Lauber, aluminate and citrate of soda, and glucose and soda. Witz gave preference to a mixture of 300 grams acetate and 300 grams hyposulphate of soda, thickened with a litre of light-colored dextrine.[4]

According to Ch. Zuercher, aniline black develops badly or not at all, if the pieces after printing and oxidation are exposed to a current of cold air. The aniline

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[1] *Dingler's Journal* CCXL, p. 255. *Wagner's Jahresbericht* 1881, p. 874.

[2] " " CCXLV., p. 225. " " 1882, p. 968.

[3] *Wagner's Jahresbericht* 1882, p. 992.

[4] *Wagner's Jahresbericht* 1882, pp. 993 and 995.

appears to volatilize. The black does not develop well by oxidation at a lower temperature than 25°C.[1]

A preparation for the continuous oxidation of aniline black has been made by Preibisch.[2] The fabrics, allowed to float loosely in the preparation, are dried in the first and oxidized in the second stage of their passage.

The results obtained are very satisfactory.

B. Processes Having Reference to Dyeing.

The aniline black processes of Lightfoot have become of importance more particularly for printing, but the inventor pointed out their applicability to dyeing fabrics and fibres. The process slightly modified is used satisfactorily at the present time for dyeing fabrics in solid colors.

The first patent relating particularly to dyeing was that of Bobœuf[3] for "the fabrication and application of coloring matters suitable to replace blacks, blues, indigoes and other colors."

As published, this patent was a little confused, the theoretical considerations showing that the author is hardly a chemist in the scientific sense of the word, while the observations therein contained are of remarkable exactness, and give the priority to Bobœuf of placing the dyeing of aniline blacks on a solid basis.

The reason for which this process did not succeed in 1865, was not owing to intrinsic defects, but to the high price of aniline and bichromate at that time.

Thus the aniline blacks had to struggle against logwood blacks which are extremely cheap.

Bobœuf's patent is too long to reproduce *in extenso*, so we give only the most important portions.

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[1] *Bulletin de la Société Industrielle de Mulhouse* 1885, p. 319,

[2] *Wagner's Jahresbericht* (1885), p. 978.

[3] *French Patent* 68079, July 15, 1865.

The author makes bichromate of potash to react on salts of aniline, either the ordinary salts or the acid salts, which are only the ordinary salts dissolved in an excess of acid. In the latter case he obtained colors which he considered to be formed by "double decomposition," but which really are only formed by the *oxidizing action of chromic avid*, liberated by the action of the excess of acid in the aniline salt on aniline, the double decomposition having occurred previously.

In the first case—employing ordinary hydrochloride of aniline and bichromate of potash—a brown color only was formed, and no immediate precipitation took place. If it does form in this case, it is not a product commercially available for dyeing.[1]

On the contrary, if the same solution is made with *chromate of potash*, a yellowish oleaginous precipitate is formed, which also does not form a utilizable coloring matter.

"But if instead of proceeding thus, an acid is previously added to the hydrochloride of aniline, in this solution with chromate or bichromate of potash, a blue or dark green precipitate, etc., or presenting an intense black color is formed, according as more or less the hydrochloric acid and the chromate are employed, or one or the other of the salts be in excess, or more or less of the acid or salt of aniline be added."

The author adds: "When the color is formed, it is sufficient to pass the fabric (silk, wool, or other animal substances, cotton, hemp, linen, or other vegetable or woody substances), through the salt or salts which are capable of forming a precipitate with salts of aniline, the color is formed. Passing for example the stuffs or fabrics through chromate or bichromate of potash, etc., (in

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[1] With normal hydrochloride of aniline and bichromate of potash, a precipitate of bichromate of aniline is formed in sufficiently concentrated solutions.

order to improve the color without impairing the fibre, the directions for use state that it is to be passed through a second bath), and finally soaked in the salt of hydrochloride of aniline. The process may be reversed where judged to be convenient or necessary. Thus, the fabric may be passed through hydrochloride of aniline and afterwards through chromate or bichromate of potash.

..... "The chromates and more particularly the alkaline bichromates produce blue colors, which after rinsing with water produce a most beautiful black color (which may be replaced advantageously), when not in excess, by dark green precipitates, when the chromates are in excess.

"With oxalate of aniline a *maroon-black* precipitate is given. With the arseniate a black like India ink, by reacting on the chromate or bichromate of potash.

"Each aniline salt gives a black with a peculiar reflex. The yellow and red prussiates give blue and green colors, clear and dark with the ordinary and definite salts of hydrochloride of aniline, however, others may be prepared with other salts, particulary those containing an excess of acid.

"From what has been explained, it will be understood that fabrics may be equally colored or precipitates obtained by means of an ordinary or neutral salt of aniline and a salt (chromate or bichromate for example), *which does not by itself give a precipitate*, and then rinsing in *acidulated water* OR BY ADDING AN ACID TO THE MIXED SOLUTION."

Bichromate of aniline is therefore first formed and then oxidized by passing through an acid, or the dyeing is effected directly in A SINGLE BATH, with a salt of aniline, bichromate and excess of acid, as is done in practice at the present time.

"The dark colors obtained by these processes certainly appear black, but they are, nevertheless, mixtures of different colors (blues, greens, reds, etc.), the reflex

varying particularly with the procedure used, the salts employed, or the rinsings or washings in alkalis or various salts used, etc., etc.

"The various shades produced may be derived or compounded, by mixing two or more salts *which do not mutually precipitate* (chromates and prussiates of potash for example), and afterwards precipitating them by acid or neutral salts of aniline.

"A multitude of shades and various combinations are thus obtained.

"This new method of producing various colors and shades presents great advantages to *skillful and intelligent* dyers, etc., who will be enabled to produce new shades for the contractors, more readily than the unskilled can reproduce those already made."

The last assertion has been fully confirmed by the experiments of Chas. Girard, Magnier de la Source, and Ogier,[1] who, having given the text of Bobœuf's patent to various dyers, they obtained the most beautiful blacks.

Bobœuf's process at the hands of the dyers of the north of France has become at once very simple and very economical in practice.

See the following details of the process, which we give for the convenience of those engaged in the industry:

Prepare two solutions separately, one of 6 kilos aniline, 9 kilos hydrocholoric acid, and 12 kilos sulphuric acid in 200 litres water; the other of 12 kilos bichromate of soda, also in 200 litres water. Place in a small vessel 2 litres of each solution, and work in it quickly one kilo. of cotton. The black develops in two minutes; it is a bronze-black.

As fast as each kilo of cotton is dyed, dry it, and steam at ¼ atmosphere for 20 minutes. By this opera-

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[1] *Consultation technique pour des teinturiers de France sur la valeur des brevets de M. S. Grawitz*, Paris, 1877, pp. 35–42.

tion the bronze-black becomes a true black, and practically not subject to greening. Soap and wash.

This process is now in use in the dyeing establishments of the north of France.

In regard to steaming, the dyers in question have profited by the observations of various chemists, among other, those of G. Witz, in 1874, that the black oxidized at a high temperature resists better the agencies which produce greening, than that formed at only a low temperature.

Shortly after Bobœuf, Alland took out a similar patent[1], for first working the fibre in a solution of bichromate of potash, then in another very acid bath containing common salt and hydrochloride of aniline, by passing the textile material many times through these two baths, the deepest and most beautiful black is obtained. The black deposit which forms in the baths can be filtered and employed as a paste color in printing.

Alfred Paraf[2] has taken out a patent in which he claims the use of chromate of chromium (brown oxide of chromium), for producing aniline blacks for printing or by dyeing. The principal passages are as follows:

"I prepare the textile fibre with a soluble salt of chromium, the chloride for example, then without washing pass it through a solution of soda or another alkali, then through a neutral solution of chromate of potash or soda, I then wash, etc. In this manner I precipitate on the fibre the insoluble brown binoxide of chromium, I then work it in a solution of an aniline salt containing 2½% of a chlorate, expose it for oxidation, and treat in the same manner as steam-black.

The final claims of Paraf's patent are as follows:

"*First.*—The employment of chromic acid as an oxidizing agent in printing by one operation (operating

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[1] *Bulletin de la Société industrielle de Rouen*, 1874, p. 172–175.

[2] *French patent* 71692, May 24, 1866.

under the conditions described in this application) by the use of insoluble or partially soluble salts of chromium, capable of liberating chromic acid under the conditions indicated in this application, as for example the brown binoxide of chromium or chromate of chromium, *chromate of sesquioxide of iron*, subchromate of lead, or among more soluble salts, the chromate of chromium and manganese, chromate of manganese, etc."

"2d. For the production of black from aniline or analogues of aniline."

"3d. For the production by oxidation with chromic acid of all the colors produced in printing, which up to the present time have been produced by two operations."

"4th. As mordants for reds, blues, or other madder colors, either alone, or combined with a chlorate."

On November 8, 1865, Paraf-Javal took out French patent, 69254, for 'the manner of utilizing the properties of certain bodies in order to obtain novel results, or results already known in a more advantageous manner.'"

The author remarks that many bodies react on each other in too rapid a manner for convenient use; for example, chromic acid on aniline or toluidine. *The action is rendered more feasible by stirring, and also by diluting the bath containing the chromic acid and the substance generating the color, aniline for example, and repeating the dyeing for as many times as is requisite to arrive at the desired intensity of color;* or it is well to neutralize the dye-bath as nearly as possible, it being only requisite to follow with an acid bath; or, as well, by cooling sufficiently to retard the reaction. In the last case, the fabric becomes colored immediately on taking from the bath.

According to Paraf, the blacks and greys thus obtained by the action of chromic acid on aniline are different from those obtained by the other known processes, in that they are neither turned green by acids,

nor are soluble in essential or saponifiable oils, or in carbolic acid, or in aniline. The process remains in principle the same as that of Bobœuf, notwithstanding certain differences: Bobœuf speaks of the *instantaneous* production of the black in an evidently concentrated bath; Paraf-Javal dilutes the bath containing the elements generating the black, and allows it to develop gradually.

Paraf-Javal thus claimed in 1866 the employment of a single bath, containing the same elements as those which Grawitz claimed nine years later. Paraf-Javal heats the bath *at the end of the operation*—the employment of heating being claimed in 1874—but in a more explicit manner by the process of Grawitz's patent in 1877.

In 1886, Lightfoot having observed that the color develops badly on wool, by reason of the reducing action of the fabric, he subjected it previously to the oxidizing action of hypochlorous acid (1 kilo 300 grams of a solution of chloride of lime, 180 grams hydrochloric acid, and 60 litres water, working the wool in it for 20 or 30 minutes at 38° C.). The fabric is then dyed with Lightfoot's or printed with Lauth's black, and sulphate of copper.

In the same year Higgin[1] recommended the preparation in the fabric of an insoluble chromate, chromate of copper, for example, and then printing with an aniline salt, with which it appears to have a natural affinity.

Carves and Thirault[2] claimed the employment in dyeing and printing of *greys soluble in boiling water, resisting acids and soap, obtained directly from aniline and its homologues*, which they designate by the generic name of *mureines*, and which are obtained by the action of bichromate of potash, a salt of iron, and

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[1] *French Patent* 73054, Sept. 26, 1866.

[2] " " 73345, Nov. 5, 1866

an acid, on a solution of an aniline salt in an excess of acid.

Reimann[1] gave the following process for dyeing cotton with aniline black: Treat with a soluble salt of oxide of chromium, pass without washing into carbonate of soda, then into chromate of potash, in this manner fixing the insoluble chromate of chromium; dye in a solution of an aniline salt, adding 2½% of a soluble chlorate, press, allow the color to oxidize until the shade is a deep green, and then pass into bichromate to develop the black.

Persoz[2] proposes to dye wool in aniline black, mordanting in a mixture of bichromate of potash (5 grams), sulphate of copper (3 grams), sulphuric acid (2 grams), and water (1 litre), boil for one hour, rinse, and pass into another bath containing oxalate of aniline of 1° or 2° Bé. "The proportions of the mordant and dye-bath are not absolute, *except as to the nature of the salts employed.*

In his English patent 2843, of Oct. 9, 1867, Persoz says, among other things, that the passage through the aniline salt should be made hot, the order of the operations may perhaps be inverted, first charging the wool with an aniline salt, then passing through *hot* bichromate of potash, finally plunging into a cold bath containing at once a salt of aniline and a chromate (*dyeing in a single bath*).

For cotton, the same author[3] claims, first, the fixing on the fibre chromate of lead, and then dyeing in a salt of aniline properly acidulated.

Dr. Reimann[4] recommends for dyeing wool and silk,

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[1] *Wagner's Jahresbericht* (1869) p. 615. *Die Färberei der Gespinnste und Gewebe.* Berlin, 1867, page 272.

[2] *French patent* 77607, Aug. 23, 1867.

[3] *English patent* already cited.

[4] ELSNER'S *chemisch-technische Mittheilungen* 1867–1868, p. 44.

working the fabric in a *hot* solution containing sulphate of copper (500 grams), chloride of potash (150 grams), bichromate of potash (250 grams), and water (5 litres), then dying in any salt of aniline, and repeating the operations until the black is sufficiently intense.

Gonin and Glanzmann[1] propose for printing or dying aniline black on wool or silk, a mixture of 100 grams chlorate of potash, 100 grams sal ammoniac, 250 hydrochloride of aniline (or another salt of aniline or its homologues or derivatives), and 125 grams nitrate of aniline of 50° Bé. (or another salt which induces or favors oxidation).

The color is developed by exposure, preferably in conjunction with heat and moisture. For printing, the color is suitably thickened, printed, and developed in the same way.

Lauth[2] proposes a general method for fixing on fibres the higher oxides of manganese, subsequently passing into an acid solution of an aniline salt.

Lauth mordants vegetable fibres, more particularly by a process long used industrially in making *bistre*, and animal fibres with the assistance of alkaline manganates or permanganates.

The dye-bath is composed of 1 litre water, 50 grams aniline and 100 grams hydrochloric acid.

"The concentration of the mordant, that of the dye-bath, the nature of the acid, that of the base (aniline, toluidine, cumidine, naphtylamine, etc.), varies according to circumstances and the shade which it is desired to attain, and which may be varied from blue-grey to violet-brown, or even the most intense black.

"In modifying this process, that is to say in mixing regenerated or precipitated black oxide of manganese with a neutral salt of aniline and and ammonium salt,

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[1] *French Patent* 82552, September 24, 1868.

[2] *French Patent* 85554, May 5, 1869.

or of any other agent capable of decomposing black oxide of manganese, under the influence of steaming, the color on printing and steaming also develops black.

" The sesquioxide and black oxide of manganese of which I have thus far spoken exclusively, may be replaced *by other metallic oxides or acids rich in oxygen*, for example, plumbic acid,[1] or by certain salts, such as the manganates or permanganates (of baryta, copper, etc.), chlorite of lead, etc.

" It will be seen, therefore, that for mordants I prefer the application of insoluble substances rich in oxygen or in chlorine, susceptible of very easy decomposition, and in consequence capable of developing aniline black by a single operation on an acid solution of aniline.

" The insolubility of these mordants presents the advantage of easy combination with the articles to be dyed, and also avoids the diffusion of the color in the dye-bath, developing the color on the fibre itself instead of provoking its formation in the bath, as results in the processes thus far published."

In the amended patent of October 15, 1869, the author adds :

" On taking from the bath, I wash the fibres in running water until all the acid has been eliminated, which is easily ascertained, it being well known that aniline blacks turn green in presence of acids.

" The fibres or fabrics are then to be dried immediately.

" The shades thus obtained can be modified at will by a new method of development or oxidation, which consists in passing the fibres or fabrics through a lukewarm or boiling solution of a number of substances, the nature and concentration of which is determined by the shade and intensity of tone which it is desired to produce. I cite, among others, chloride of lime, *salts of*

[1] Peroxide of lead.

chromium, of copper, OF IRON, and *of mercury, either alone or associated with chlorate of potash, ferricyanide of potassium*, CHROMATES," etc.

In a very interesting article published in the *Moniteur Scientifique* of 1873, page 794, Lauth gives the most ample details of his process, particularly insisting on the development.

"The shades obtained by dyeing may be subsequently modified or augmented in intensity by means of various agents; this fact appears curious to me; it seems to indicate that at the moment when the black oxide of manganese terminates its action, *the coloring matter produced, and which possesses all the properties of black, is still, nevertheless, in an intermediate state, and that a subsequent oxidation, is useful in bringing it to a definite state.*

"Bichromate of potash, 1 gram per litre, the salts of copper, of chromium or of mercury, especially if mixed with chlorate of potash, or a salt of copper and sal ammoniac (1 gram of each substance per litre), particularly increases the intensity of the black."

This passage ought to succeed the washing following the dyeing, *and be prolonged for half an hour at the boiling point.* This is followed by washing with water and boiling with soap.

"The process I describe gives strong, beautiful blacks, *absolutely fast*, does not weaken the fibre, and is prompt."

By developing with a chromate or hypochlorite and heat, Lauth's blacks become exempt from greening; it, moreover, becomes so *immediately* on dyeing in an acid solution of aniline salt *at a temperature above 75°* C.[1]

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[1] Compare on this subject, CAMILLE KŒCHLIN, *Proces-verbaux du Comité de Chimie de Mulhouse*, June 14, 1882, *Bulletin de* 1882, p. 63, *des Proces-verbaux.*

If the fibre is dyed *in the cold* and then *steamed*, it does not become green more sensibly. .

The process of Lauth on its first announcement did not have all the success it merited, but has finally attained it, not so much for dyeing fabrics in solid colors, as on a great scale for the development of "*bistres rongés*" from aniline or naphtylamine.

In 1870 and 1871, Gonin of Rouen *practiced and made over to various houses* a process for dyeing black, consisting of passing the cotton through two baths, the first containing 1 kilo hydrochloride of aniline, 1 kilo hydrochloric acid, 600 grams crystallized choloride of copper, 600 grams chlorate of potash, and 80 litres water, (for 10 kilos cotton); and the second of 1 kilo bichromate of potash, 500 grams sulphuric acid, and 80 litres water. The two baths being replenished gradually with solutions of the same elements as they became exhausted.

This process was not made public at the time.

In 1871 Persoz[1] succeeded in practically obtaining a black by a method of separately applying bichromate of potash and a salt of aniline.

Upon the fabrics prepared in salt of aniline and pressed, he subsequently applied the other compound by pulverization. The nature of the acid, according to him, may be varied (he particularly recommends a mixture of hydrochloric and sulphuric acids), according to the concentration of the solutions, and their degree of acidity, finally heating, in order to obtain the color immediately, or, on the contrary, retarding the action which is only completed by exposing the stuff to a hot atmosphere. In all cases it is so arranged, that the cloth enters white at one end of the machine and comes out black at the other.

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[1] *Moniteur Scientifique* 1872, p. 396; *Wagner's Jahresbericht* 1872, p. 710.

Persoz adds that the same method slightly modified, according to the nature of the materials employed, gives good results for wool.

On June 3, 1872, Jarosson and Mueller-Park took out patent (French) 95512, according to which they mordant in protochloride of iron of 12° Bé. during two hours, allowing the mordant to oxidize itself for twelve hours, then passing *through very acid hydrochloride of aniline and chlorate of potash, then* placing in an enclosed revolving apparatus for five hours and at a temperature first of 30° and gradually increasing to 50° C. It is then allowed to remain extended in the apparatus for some hours, then passed through acidulated bichromate at 50° C. for twenty to thirty minutes, and lastly washed.

Nahrath and Firmenich, of Geneva, from the spring of 1873, furnished to their customers a process, which consisted in passing the fibre quickly through a bath of hydrochloride of aniline with the addition of tartaric acid, then passing after squeezing through a bath of bichromate and hydrochloric acid, allowing it to remain many hours in that oxidizing agent, finally returning to the first bath (a salt of aniline), thus alternating successively until an intense black was obtained.

Tantin and Brière[1] proposed to dye aniline black, mixing *in a single bath* a very acid salt of aniline and black oxide of manganese, working the fibre for three hours, and finally passing the very dark green cotton through a bath of bichromate.

Pinckney[2] specified a method of employing the salts of vanadium and uranium in dyeing and printing, after Lightfoot had first announced the advantages of these metals in 1871. In order to dye *in a single bath*, he recommended taking 150 parts hydrochloride of aniline,

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[1] *French patent* 101685, Jan. 5, 1874.

[2] *French patent* 102050, Feb. 2, 1874.

one-eighth a salt of vanadium, 20 chloride of nickel, 108 chlorate of potash, 2500 of water.

The fibre is plunged into *the mixture of these substances*, or as well proceeding by *successive immersions*, at first in the metallic bath, and then in a bath containing the salt of aniline and a chlorate.

The dyeing may be effected at ordinary temperatures, but a *higher temperature* would sometimes be advantageous.

We finally notice, although not published at the time, a process found out by Bretonnière, of Laval, and sold to J. J. Muller-Pack, June 27, 1873.

"The following solutions are prepared:

"Light aniline oil, 1 litre; hydrochloric acid of 22° 2 kilos; hot water, 10 litres; and bichromate of potash, 1.2 kilos in 10 litres hot water.

"Prepare (for 10 kilos cotton) a bath of 90 litres and heated to 60°, add 2 litres of the solution of aniline, enter the cotton and allow to remain ten minutes; on adding 2 litres of the bichromate solution and allowing to stand for ten minutes, a grey tint is obtained. Again, add 2 litres of the aniline solution and leave for ten minutes, and afterwards 2 litres of the solution of bichromate, and continue the process in the same order. The cotton is then a deep bronze black; add 2 to 300 cc. hydrochloric acid, allow to stand five minutes; then take out the cotton and wash for ten minutes in a large quantity of cold water, containing 50 cc. sulphuric acid; finally rinse thoroughly in hot water.

"After washing it can then be soaped. The black thus obtained is very beautiful and does not turn green."

M. de Vinant[1] dyed cotton fibre with aniline black by passing through sulphate of copper acidulated with hydrochloric acid, then through hydrosulphide of

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[1] *Moniteur de la teinture* (4) I, p. 67.—*Wagner's Jahresbericht* 1873, p. 837.

sodium, then through a solution of sal ammoniac, chlorate of potash and pyrolignite of aniline, and finishing in bichromate of potash.

Lamy[1] stated that aniline black is, however, faster and less subject to greening in proportion to the degree of oxidation; the violet-black, obtained by working in bichromate and then in hypochlorite of soda, being more refractory to washing and acids than the blue-black obtained by passing through soda.

According to G. Witz[2] tissues dyed or printed with aniline black may be bleached by first passing through an acidulated solution of permanganate of potash, and then through oxalic acid.

On September 30, 1874, S. Grawitz took out his first French patent, 105130, for the "processes employed in the production of aniline black;" on October 3 of the same year, the first amendment (*certificat d' addition*) to this patent; on November 3, two other patents, Nos. 105554 and 105555, relating to the same subject.

The patents of Grawitz have given rise to so many law suits and scientific and industrial discussions that we have devoted a special chapter to them. We shall reproduce them *in extenso*, and discuss their value from our point of view, sustaining ourselves by the experience of various authors, as well as by our personal experiments.

Coquillion[3] describes processes for obtaining black bases, by the action of salts of iron on salts of aniline in presence of chlorates. The following recipe is given for dyeing: "For 20 kilos of dry cotton, take 3 kilos aniline, and 4 kilos hydrochloric acid of 20° Bé. Mix the two liquids and allow to cool. Then add 2 kilos chlorate of potash, dissolved in 30 to 55 litres of water,

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[1] *Wagner's Jahresbericht* 1874, p. 888.

[2] *Bulletin de la Société industrielle de Rouen* 1874, p. 100.

[3] *French patent* 106031, March 10, 1876.

mix well, and finally add 35 litres chloride of iron of 20° Bé. Immerse the cotton in the mixture, and allow it to remain eight to twelve hours at the surrounding temperature."

After about this time remove from the bath, and immerse in a solution of carbonate of soda of 10 to 15° Bé. This bath is for removing the excess of acid. Then wash the cotton and take it to a bath of bichromate of potash heated to 40°–50°, and containing about 200 grams of this salt dissolved in 30 to 35 litres water. This bath is *to give fastness to the black and prevent greening.*"

" The cotton may be left here for half an hour, then washed, wrung out and passed into a final softening bath, composed of 0.5 kilos of *huile tournante* (Gallipoli oil), and 1 kilo. carbonate of potash, dissolved in 30 to 35 litres of water."

The second *certificat d' addition* to Grawitz's patent 105130, bears date of April 29, 1875. According to patent 109193 of August 23, 1875, Leriche accomplished the dyeing of cotton by successive passages, first through a hot mixed solution of chlorate and bichromate of potash, and then through an equally hot solution of sulphate of aniline. These passages are repeated many times.

In 1875 Ladureau proposed to impregnate cotton with a solution of chloride of manganese, chloride of iron, chloride of potassium and a salt of aniline, allow to oxidize for twenty-four hours, and then pass without rinsing into a bath containing about 1 % bichromate of potash, cold or better heated, to develop the black.

According to a Bavarian patent, L. Wagner,[1] dyed cotton fibres dark blue in the following manner.

A paste is made by heating a solution of ½ litre glucose, 40 grams starch and 40 grams chlorate of potash;

[1] *Wagner's Jahresbericht,* 1875, p. 992.

dissolve separately in ½ litre of a glucose solution, 80 grams hydrochloride and 13 grams sulphate of aniline; and finally, in two litres of the same liquid, 40 grams chloride and 13 grams sulphate of copper. Mix the three solutions, pass the cotton through it, wring, leave it piled up for 1 hour, then oxidize for 4 to 5 hours by moisture and heating at 30° C. Then pass through dilute milk of lime, then through dilute hydrochloric acid, then through carbonate of soda or soap.

The addition of glucose, an oxidizable body, to the bath, no doubt retards the oxidation of the aniline, and arrests it at the formation of the blue, emeraldine.

In an interesting memoir on the action of vanadium in the formation of the black, Antony Guyard (Hugo Tamm),[1] a paper to which we shall again refer in discussing the theory of the formation of the black, says among other things "*that aniline black is nothing but dehydrated emeraldine; that a high temperature in the oxidizing room is necessary, not to form the emeraldine, but to dehydrate and transform it into black; that the emeraldine may be dehydrated even in the liquid in which it is formed, this transformation into aniline black being effected by heating the liquid, in the same manner as the blue hydrated oxide of copper is converted into the black oxide* BY BOILING."

On April 7, 1876, Jeannolle took out a patent (French) No. 112132, for obtaining a *dark blue* dye that replaces aniline blue or indigo, and suitable for using in an economic manner instead of the pure vat-dyed indigo blue. For 100 kilos. cotton, Jeannolle took 1,600 litres water, 5 kilos. hydrochloric acid, 12 kilos. sulphuric acid, 5 kilos. aniline, and 5 kilos. bichromate potash, dyeing in the cold for one hour; wash, and remove the last traces of acid in a slightly alkaline bath at 40°.

On June 2, of the same year, Hommey[2] performed

[1] *Bulletin de la Société Chimique de Paris* XXV, 1876, p. 58.

[2] *Bulletin de la Société industrielle de Rouen* 1876, pp. 263-266.

the dyeing of black by the use of 1,000 grams water, 80 grams hydrochloride of aniline, 40 grams chlorate of potash, 5 grams hydrochloric acid, and 0.1 gram vanadate of ammonium. The color is developed by exposure, and the black fixed by a hot bath of bichromate.

Gouillon, in the *Moniteur de la Teinture* of July 5, 1876, published the following observation :

" In order that aniline black may be perfectly fast and not liable to become green, it is necessary *that a high temperature be employed* in some stage of its production. However, if it be exposed in a hot oven at 40°–50°, it endangers the strength of the fabric. *It is preferable, after oxidation, to pass the cotton into a boiling solution of bichromate of potash.*"

Aug. 24, 1876.—First *certificat d'addition* to Grawitz's patent, 105554.

On October 13, 1876, John Bryson Orr took out a French patent, 115003, for the prevention *of the greening of aniline black.*

" When the fabrics have been printed and fixed for twenty-four to forty-eight hours, as is customary in printing they are treated as follows :

1st.—Pass through a boiling bichromate of potash bath (112 grams of the potash salt to 4½ litres water).

" A little acid added to the bath is an advantage, as it aids in liberating the chromic acid.

" Chromic acid of an equivalent strength may be substituted for bichromate of potash.

" The fabrics should be passed through the bath on rollers, the passage lasting less than a minute.

" 2d. Wash the fabrics with boiling soap and water.

" 3d. They are dried.

" 4th. Then submit them to a cold bath of chlorate of alumina or another chlorate, such as chlorate of ammonium (containing one part of the salt to sixty parts water.

" 5th. Again dry the fabrics.

" 6th. Then submit to the action of steam for about half an hour, *or the treatment with steam may be omitted, if the pieces are worked for half-an-hour or an hour in boiling chlorate of alumina or some other chloride, such as chlorate of ammonium, containing one part of the salt to 100 parts water.*

" 7th. The bichromate bath may be preserved and employed many times in succession.

" 8th. It is preferable to submit the fabrics or yarns to steaming as soon as possible after the drying which follows the chlorate bath.

" 9th. Care should be taken that the chlorate bath is not too strong, one part in sixty (or one per cent. for the lighter fabrics) is recommended as sufficient.

" 10th. The process herein recommended, not only *preserves the tissues from greening, but renders the blacks more perfect*, and the whites purer.

" *The same process may be employed for dyeing fabrics*, but in this case the chloride bath should be weaker.

" Besides chlorate of alumina, it should be understood that other chlorates, which are decomposed by steam without the presence of an acid, may be employed as above indicated.

" In conclusion I claim as my invention and desire to pveserve the exclusive property in :

" The treatment of *dyed or printed fabrics* with aniline black, so as to prevent what is known by the name of greening."

October 21st, 1876.—Grawitz's fourth French patent, 115160: THE PRODUCTION IN DYEING AND IN PRINTING OF AN UNALTERABLE ANILINE BLACK.

The following is the patent of Kœchlin Bros., made public at the meeting of the *Société industrielle de Mul-*

house on November 29th, 1876, a sealed statement of which was deposited on April 9th, 1876.

ANILINE BLACK.

Process of Kœchlin Bros., to prevent the greening of that color.

"Aniline blacks, submitted to the action of acid reducing agents, such as sulphurous acid or sulphuretted hydrogen (either in solution or the gaseous state), assume a greenish color, and are re-transformed more or less completely into emeraldine, which is dark blue in the alkaline state, becoming green with the slightest traces of acid.

"There exists a more highly oxidized product than aniline black, which is not transformed into emeraldine by alkaline or acid reducing agents, and is obtained in the following manner:

"The aniline black, printed and fixed, is finished in the ordinary manner, then submitted in a vat *to an acid oxidation at a higher temperature* than 75° C. It only remains to wash and soap the pieces.

"Among the oxidizing agents, which give the best results, we specify: *salts of peroxide of iron, chromic acid, certain easily decomposible chlorates, such as chlorate of alumina, etc.*

"The ferric solution is prepared by adding to a persalt of iron, 1 to 1½ times its weight of 66° sulphuric acid, in order to prevent the oxide of iron from becoming fixed on the fabrics. The solution is employed in the proportion of 1 to 2 grams per litre, in a vat for six or eight pieces, working it therein for *half-an-hour or an hour at 80° C.*

"The ferric salts being of less usual occurrence in commerce than the ferrous salts, we prepare a solution as follows:

Dissolve 20 kilos. copperas in
60 to 70 litres water ;
add to it
5 kilos. bichromate of potash,
15 to 18 litres 66° sulphuric acid.

" It is necessary to employ this quantity of water, on account of the heating of the liquor by sulphuric acid and the slight solubility of acid ferric sulphate. Take 4 to 8 litres of this liquor and operate as before.

" For *black and orange* styles *chromic acid* may be used in the proportion of 300 to 400 grams per vat for 6 to 8 pieces (or 300 to 400 grams bichromate and a quarter of a litre of sulphuric acid), otherwise operating as in the case of iron. The orange is then restored in an alkaline chromate."

N. B.—" For solid black and blue styles, it is necessary to have a slight excess of the ferrous salt in the liquid (for chromic acid destroys the blue). Using the above proportions, taking 4 kilos instead of 5 kilos of bichromate."

Delory[1] describes the dyeing of wool and silk with aniline black. He mordanted 250 grams of wool with 100 grams bichromate of potash, 100 grams sulphuric acid and ten litres boiling water, allowed to cool in the bath, and afterwards dyed with thirty grams hydrochloride of aniline and fifty-five grams bichromate in ten litres water, at first cold, and then raising to 95°–100° C. For silk the mordanting bath is weaker, and only raised to 60°–70°.

Theilig and Claus, of Crimmitschau, Saxony, impregnate the cotton in skeins or yarn, according to German patent No. 9804, with hydrochloride of aniline, chlorate of potash or another oxidizing agent, and chloride of vanadium. The materials, freed from liquid, are exposed in a closed apparatus to a current of hot air, in

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1 *Wagner's Jahresbericht* 1879, p. 1068.

which is more slowly mingled the vapor of water. In this way the oxidation of the aniline is rapid and complete and the acid vapors are removed. Then the goods are passed through bichromate of potash or an alkali.[1]

Prud'homme, in 1885, introduced industrially a process for removing undeveloped aniline black. The fabric is placed in a mixture of basic hydrochloride of aniline, chlorate and ferrocyanide of potassium, and a trace of vanadium, then dried. Then print with an alkali or an alkaline salt, acetate or carbonate of soda or of lime, and proceed according to Mather and Platt. In the portions printed with alkali the black is not developed, finish by washing and a passage through bichromate. In adding the salts in question to a color made plastic and thickened with albumen, colored designs are obtained on a black ground.

Rettig[2] has studied the action of black oxide of manganese fixed on fabrics, on the homologues of aniline. Orthotoluidine gives a blue-black, metatoluidine a plum color fast to soaping, paratoluidine, as well as the xylidines and higher homologues containing methyl in addition to amidogen, give cashoo-shades which do not resist soaping.

Gilliard, Monnet and Cartier, of Saint-Fons, employ in dyeing a non-greening black, a mixture of hydrochloride of para-phenylène-diamine, hydrochloride of aniline, an alkaline chlorate, and vanadium. The cotton is impregnated with this solution and the color develops in twenty-four hours at the ordinary temperature.

We have already seen that in extending the process for aniline black to other bases, orthotoluidine give a more violet-black, α-naphtylamine a puce, β-naphtylamine a brown, para-phenylene-diamine a dark brown, and benzidine an orange brown.

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1 *Wagner's Jahresbericht* 1880, p. 785.

2 *Bulletin de la Société industrielle de Mulhouse* 1886, p. 174.

The applications of these bases are not very imporant, the puces of *a*-naphtylamine have been abandoned on account of the bad odor of the base.

THEORY OF THE FORMATION OF ANILINE BLACK.

We have already seen from what precedes that aniline black is formed by the dehydrogenation of aniline. This dehydrogenation is effected by the action of the most widely differing oxidizing agents, oxygen derivatives of chlorine, chromic acid, per-salts of iron, black oxide of manganese, etc.

Chloric acid does not transform aniline into black; a solution of chlorate of aniline may be boiled without decomposition, but if a drop of acid be added, or a little of a salt of a metal, the chlorate of which is easily decomposable (vanadium, cerium, copper, manganese, iron), the black is formed. Chloric acid is then decomposed and its reduction products oxidize the aniline.

From the result of Lightfoot's experiments, it was long believed that the presence of a metal having many degrees of oxidation was necessary to the formation of the black. It was found that the chlorate transformed the metallic salt into the state of maximum oxidation, and that this oxide, oxidizing the aniline, was reduced to the lowest oxide, that it was again reoxidized by the chlorate, and so on. This theory has been sustained by many chemists, and in particular developed by Anthony Guyard.[1]

Grawitz also adopted it in his *certificat d'addition* to French patent 105130, Apr. 29, 1875.

[1] *Bulletin de la Société chimique de Paris* XXV., p. 58.

Rosenstiehl,[1] on the contrary, has demonstrated that this is not the function of the metallic salt, but rather that of decomposing the chloric acid, and that it is the chlorine and the oxygen derivatives of chlorine which oxidize the aniline to emeraldine, and afterwards to black.

In a series of demonstrations remarkable for their precision and their logic, he has shown in a most conclusive manner, that black can be obtained by the action of the oxides of chlorine without the intervention of a trace of metal.

The electrolytic experiments of Coquillion and Goppelsrœder also show that the intervention of a metal is not necessary to the formation of black.

That is to say, the theory of the many degrees of oxidation of the metal is entirely erroneous. We do not believe that. We think, on the contrary, that under the conditions the two reactions can take place simultaneously. If aniline be oxidized by chloride of copper and an insufficient quantity of chlorate, the mixture contains, after the formation of black, cuprous chloride.[2]

Like the chlorate, the bichromate of aniline in a pure state is relatively stable, but if acid is added to a solution of the salt, the black forms immediately. It is on the fabric as a solution. The cotton plunged into a solution of bichromate of aniline is not dyed, but the black is developed on adding an acid.

On this fact, *no black without acid*, rest many of the methods for making preparations of aniline black. The elegant process of Prud'homme (p. 77) is a very interesting application.

The blacks formed by *exposure to air* are to be distinguished from the blacks formed directly. This leads

[1] *Bulletin de la Société industrielle de Mulhouse* 1876, p. 179.

[2] NIETZKI, *Organische Farbstoffe*, 2d edition 1888, p. 146.

us to the belief that this is the principal difference between the two kinds of black. The airing is, in our opinion, only useful in allowing the oxidizing agent time to exert its action on the aniline; the solution in which are the elements necessary to produce the black, becoming concentrated by the evaporation of water, the oxidation then going on gradually in the interior of the fibre. The oxidation in the air does not appear to play any other part. The airing may be replaced by elevation of temperature; thus the blacks of Lightfoot and vanadium blacks, which develop in one or two days by exposure, can be finished in some minutes by steaming (p. 53).

GREENING OF ANILINE BLACK.

By the action of oxidizing agents on aniline are formed a series of different products, which may be dividend into three classes.

1st. The least oxidized derivative, which has been usually called "*Emeraldine.*" This body in the basic state is blue and in the acid state a vivid green. It is soluble, *at least partially*, in alcohol, glacial acetic acid, etc. Concentrated sulphuric acid dissolves it with a violet-red color.

This body is probably identical with that formed by the oxidation of a mixture of one molecule of para-phenylene-diamine and one molecule of diphenylamine, or of equal molecules of para-amido-diphenylamine and aniline. Caro has obtained by the oxidation of free aniline by an aqueous solution of permanganate of potash, extracting the yellow liquid with ether, and treating with an acid, a derivative which, separated, had analogous properties.[1]

The bodies obtained by Emile Kopp (pp. 9–15 of this memoir), in all cases contain this substance in large quantitlies. We do not know the composition of "*Emeraldine*"; probably it has never been obtained in a state of purity, but always mixed with "*Nigraniline.*"

2d. By the subsequent action of these oxidants on emeraldine, the aniline black, properly called "*Nigraniline*, if we retain the name of Rheineck, is formed.

[1] NIETZKI, *Farbstoffe* 1888, p. 168.

This body is insoluble in the usual solvents, slightly soluble in aniline and phenol, with a very dark indigo-blue inclined to violet; the salts are also green, but of a much more somber green than those of emeraldine.

This is the nigraniline analyzed by Nietzki, Kayser and Groppelsrœder, and the formula of which is a polymerization of C_6H_5N.

A chlorinated nigraniline has been obtained by Liechti and Suida (see pp. 33–35).

This nigraniline undoubtedly forms the principal part of ordinary blacks, and it is certainly contained in the less oxidized products, the *Emeraldines*.

Nigraniline becomes green under the influence of acids, particularly sulphurous acid. This last acid, which is an energetic reducing agent, tranforms nigrani line in part or entirely into emeraldine.

3d. Finally, the non-greening black (*noir inverdissable*), a more highly oxidized product, is formed by the action of oxidants with heat, or even under certain conditions in the cold, on nigraniline. It does not turn green under the influence of acids, probably because it does not form salts, nor under that of sulphurous acid. Acid protochloride of tin reduces it to a leuco-derivative, which, however, by reoxidation, regenerates the non-greening black.

The only analyses of the non-greening black which we possess are those of Liechti and Suida (pp. 36 and 37). According to their analyses, it contains oxygen, and is capable of combining with metallic oxides (oxide of chromium). The non-greening blacks on Glantzmann (pp. 21–23) also contain this oxide.

Notwithstanding the experiments of Liechti and Suida show that the presence of metal is not necessary to prepare the non-greening black, for they have also been prepared—free and on the fibre—by oxidizing chlorinated nigraniline $C_{18}H_{14}ClN_3$, by a dilute and

boiling solution of chloride of lime. Liechti mentioned that in 1876 he had industrially converted ordinary blacks into non-greening blacks, by boiling with dilute chloride of lime, and that this agent gave him better results than chromic acid.

Aniline blacks obtained on fabrics by dyeing and printing, have in general the property of turning green under the influence of acids, especially sulphurous acid. This inconvenience is much more sensible when the aniline employed for the black is purest; the blacks obtained with heavy anilines containing ortho- and paratoluidine, or even xylidine, are much less liable to greening.

Thus the complaints of those engaged in the industry on the subject of greening, are accentuated in proportion as the aniline of commerce becomes purer. It would evidently be easy to revert to the heavy anilines, but, on the other hand, the black from pure aniline is much more beautiful. The theory of greening is easily established. Under the influence of acid oxidizing agents, aniline may give, as we have seen, many oxidation products; the first degree, *emeraldine*, is indigo-blue in the basic state, its salts are intense green; the second degree, the true black, *nigraniline*, is dark violet in the basic state, its salts are dark green; under the influence of sulphurous acid, nigraniline is reduced to the state of emeraldine.

Bichromate of potash transforms nigraniline into the chromate analyzed by Nietzki. The chromate does not turn green under the influence of non-reducing acids, but greens with sulphurous acid on account of the reducing action of that agent.

Chromic acid, acid per-salts of iron, chlorates in presence of salts of copper and sal ammoniac, acid chromates, hypochlorites, and also other oxidizing agents, transform the ordinary black into those which are con-

veniently commonly called industrially non-greening blacks. These last do not turn green *sensibly*, either under the influence of acids, nor that of sulphurous acid ; nevertheless, a black does not appear to exist which is *absolutely unalterable* by sulphurous acid and atmospheric influences.

All blacks, in whatever manner produced, may be transformed into non-greening blacks by the oxidizing agents mentioned by Lauth in his patents of 1869, and in his note to the *Moniteur Scientifique*, 1873, pp. 64–66 ; by Koechlin Bros.' process (p. 75), or those of Grawitz's French patent 115160 of Oct. 21, 1876, which are identical with those of the Kœchlins.

A curious fact is also, that bichromate of potash alone, without acid, will not render an ordinary black non-greening, while bichromate of soda will.

Non-greening blacks were first obtained at one dip by Cordillot's process, or if steam-blacks are required by Lauth's process with black oxide of manganese, for carrying on the dyeing at 75°–80°, by the processes of Bobœuf, Paraf-Javal, Persoz, and others, for first dyeing in the cold, and finally raising the temperature, or finishing the black by steaming without previous washing.

The blacks, with *a very great proportion of aniline*, appear much less liable to greening than those obtained with a smaller proportion of that base

METALLIC DERIVATIVES OF ANILINE.

As the metallic derivatives of aniline are often referred to in Grawitz's patents, it will not be useless to say a few words about them.

These combinations had been studied in a profound manner by Hugo Schiff[1] in 1864.

Long before, Hofmann had observed that aniline gave green precipitates with the sulphate or chloride of copper. The combination with sulphate of copper had been studied by Gerhardt. It is obtained on adding one molecule of sulphate of copper to two molecules of aniline, in the form of a green crystalline precipitate, which dried at 100°, has the composition $Cu\ SO_4 \times 2\ C_6\ H_5\ NH_2$, or

$$\left.\begin{matrix} N(C_6\ H_5)\ H_2 \\ N(C_6\ H_5)\ H_2 \end{matrix}\right\} Cu\ SO_4.$$

That is to say, it, the sulphate of diphenylated cupramonium,

$$\left.\begin{matrix} NH_2 \\ NH_2 \end{matrix}\right\} Cu\ SO_4.$$

On heating this compound with water, the basic salt $Cu\ SO_4 + 2\ C_6\ H_5\ NH_2 + Cu\ O$, is first obtained, together with $(C_6\ H_5\ NH_2)_2\ H_2\ SO_4$, and then the basic sulphate of copper, while the liquid assumes a red color

[1] *Ueber metallhaltige Anilinderivate*, Berlin, 1864, edited by Julius Springer.

on account of the oxidizing action of the copper salt on aniline (which, at the time of the researches of Schiff, always contained toluidine).

If *sulphate of cupranile* is treated with sulphuric acid, a mixture of sulphate of aniline and sulphate of copper is found, and these two salts do not form a double salt[1].

By the action of chloride of copper on aniline, Schiff was unable to obtain combinations (doubtless on account of the impurity of his aniline), but the compound $2\,C_6\,H_5\,NH_2 \times Cu\,Cl_2$, has been isolated by Destrem.[2] This gives with hydrochloric acid the double chloride, $2\,C_6\,H_5\,NH_2\,HCl \times Cu\,Cl_2$, analogous the other double chlorides of aniline.

The chloride of *cuivre-anile* very easily decomposes and blackens. (Schiff, p. 44 of the work cited.)

The chlorides of iron, chromium, nickel and cobalt, do not give with aniline *anilique* combinations. (Schiff.) Ferric and chromic chlorides only give a double salt with hydrochloride of aniline.

If ferric chloride be added to aniline, it first forms a basic ferric chloride and hydrochloride of aniline, with an excess of aniline and of ferric hydroxide. In the first case, the liquid soon becomes green, on account of the oxidizing action of basic ferric chloride on the salt of aniline, forming emeraldine.

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[1] Hofmann *Annalen der Chemie und Pharmacie* XLVII, p. 65.

[2] *Bulletin de la Société chimique de Paris* XXX, p. 483, 1878.

STATE OF KNOWLEDGE REGARDING ANILINE BLACK IN 1874.

Before passing to the examination of Grawitz's patents, we will briefly recapitulate the *most important* reactions and processes which were public property or included in patents prior to September 30, 1874.

1st. Blacks in Powder and for Printing.

We will include in these two headings all that relates to printing, or the production in solutions.

Runge's process: "Action of hydrochloride of aniline at 100° on bichromate of potash" (p. 7).

Perkin's process (p. 16): "Action of an equivalent of an aniline salt on an equivalent of bichromate of potash in the cold." Besides Perkin's violet, an aniline black containing chromium is found, which is stated to be employed as a paste color in printing (p. 17).

Calvert's process modified by Wood and Wright: "Concomitant and concurrent action," to quote Grawitz, "of chlorate of potash and per-salt of iron, or other oxidizing agents, on an acid salt of aniline." Wood and Wright accomplished this reaction on the fibre, but it goes without saying that it may be executed *in vitro* (p. 41).

"Action of a bichromate or chloride of lime on emeraldine," the first product of the oxidation of aniline by the decomposition products of chloric acid (p. 42).

"Action of nitrate of copper on hydrochloride of

aniline, and subsequent oxidation by bichromate of potash or chloride of lime (p. 42).

Lightfoot's process: "Action of a salt of copper and of a chlorate and an acid salt of aniline." The reaction may be made on the fabric or *in vitro* (p. 43). This process has been modified by Kopp, by replacing the salt of copper by protochloride of iron which is oxidized by the chlorate to perchloride of iron (p. 44). Camille Kœchlin replaces, in Lightfoot's method, the acid aniline salt by a basic salt (p. 46).

Bobœuf's process: "Action of bichromate on an acid solution of an aniline salt" (p. 56).

Higgin obtained the black "by the action of an aniline salt on chromate of copper (p. 47); Alfred Paraf by the reciprocal action of the salts of aniline and chlorate of potash on the chromates of chromium, of sesquioxide of iron, of lead, and of manganese" (pp. 47 and 48).

"Action of a chlorate and a salt of copper on a chloride of *metal-aniline* (a mixture of a basic chloride of iron or chromium and an aniline salt)" (Higgin, p. 48).

"Action of ferro- and ferricyanides and a chlorate on an aniline salt" (Cordillot, pp. 44 and 51).

"Action of black oxide of manganese, or other insoluble oxides or acids rich in oxygen, on salts of aniline" (Lauth, pp. 49 and 50).

"Action of the salts of heavy metals on chlorate of aniline" (Kruis, f. 50).

"Action of chlorates on aniline salts in presence of vanadium" (Guyard, p. 51).

2d. Blacks in Dyeing.

Lightfoot's process, applied by its author for dyeing as well as printing (p. 42).

Bobœuf's process (pp. 54–58): "Action of bichro-

mate of potash on an aniline salt in presence of an excess of acid."

According to Bobœuf, the dyeing may be effected either in two baths or a *single bath*, by alternate dips or a single dip.

Moreover, even if operated in two baths, it is always finished by using the single bath containing all the elements for producing the black. In effect, if the cotton impregnated with bichromate solution is passed through an acid solution of an aniline salt, or inversely, the liquid of the first is introduced into the second, and finished in a bath containing the cotton, bichromate, aniline and acid. Bobœuf particularly insists on the fact that the presence of an acid is necessary to the formation of the black.

Bobœuf does not speak of the temperature, but it seems indisputable that the dyers inspired with his ideas operated both with heat and in the cold.

The Bobœuf black formed in the cold is liable to greening, but it becomes non-greening by the subsequent treatment of Lauth, or by steaming, or by a passing through boiling bichromate without previous washing, or lastly, it becomes non-greening on heating.

The processes of Alland, Alfred Paraf, Paraf Javal, and Persoz (pp. 59–63), are based more or less on the same principles as that of Bobœuf.

Paraf-Javal indicates, in the most explicit manner, a single bath, containing aniline and chromic acid, sufficiently diluted for the two bodies not to react too strongly on each other, and he recommends "*repeating the dyeing for as many times as is necessary to produce the desired intensity.*" By heating at the end of the operation the black becomes non-greening.

Paraf-Javal, in 1867, did not speak of heating, and certainly he has not practiced it; but, from 1873, the influence of heat on the fastness of the black has

been clearly indicated, and the whole world has the right to operate in the cold, according to Paraf-Javal, and heat subsequently.

Persoz proposes some processes in two and in a single bath, and he specifies the employment of heat, it is true, in the two-bath process only.

Lauth's processes, and the improvements of the same author for rendering the blacks solid—that is to say, non-greening (pp. 63–66).

Jarosson and Mueller-Pack's process: "Formation of black by the action of a salt of iron and a chlorate on the very acid salts of aniline" (p. 67).

Tantin's and Brière and Pinkney's processes (p. 68), accomplish the dyeing at one dip in a single bath.

The influence of *heat* on the fastness of blacks had been mentioned many times: by Witz in 1874,[1] by Coquillion in 1875 (p. 70), by Guyard (p. 72), by Gouillon in 1876 (p. 73), before Grawitz had ever spoken of it.

To sum up, in our opinion colorists possessed in 1874, in patents and publications, all the elements for making the black; but they had yet to open their eyes to a practical process for its application. In fact, the methods used to-day are nearly all contained, expressly or by implication, in the documents we have cited.

The chemicals to be employed were known, hydrochloride and suphate of aniline with excess of acid, bichromate of potash, with or without the addition of metallic salts; the utility of heat in rendering the black fast was known; a series of processes were known for making solid and ungreenable, by heat, blacks obtained in the cold and sensible to sulphurous acid; in short, everything was known which Grawitz more slowly claimed as his discoveries.

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[1] Witz, *Bulletin de la Société Industrielle de Rouen* 1874, pp. 172-175.

If Grawitz had at his disposal these facts for two years and a half without putting them to a practical application, it only proves that his qualifications as a dyer leave much to be desired.

CRITICAL EXAMINATION OF THE PATENTS OF GRAWITZ.

Grawitz, as we have already seen in the preceding review, has taken out a number of patents and "*certificats d'addition*" for aniline black, principally from 1874 to 1879 :

1st. patent, No. 105130, Sept. 30, 1874.

1st. *certificat d'addition* to patent No. 105130, Oct. 3, 1874.

2d. patent, No. 105554, Nov. 3, 1874.

3d. patent, No. 105555, Nov. 3, 1874.

2d. *certificat d'addition* to patent, No. 105130, April 29, 1875.

1st. *certificat d'addition* to patent, No. 105554, Aug. 24, 1876.

4th. patent, No. 115160, Oct. 21, 1876.

2d. *certificat d' addition* to patent, No. 105554, March 22, 1877.

5th. patent, No. 124581, May 18, 1878.

1st. *certificat d'addition* to patent, No. 124581, May 7, 1879.

The first four patents and their *certificats d'addition*, which are more particularly important from the point of view of French dyeing, will be submitted to a detailed discussion; but the patents of Grawitz subsequent to 1879 will not enter into the scope of that study.

GRAWITZ'S PATENT OF SEPT. 30, 1874.

No. 105130.

For the production of aniline black on fabrics of all kinds, as well as in paste and a dry powder, suitable for employment as colors of all kinds.

My processes are based on the following reactions:

When aniline oil is made to react on any per-salt of iron or copper, there is found a salt of iron or copper aniline, which is very easily oxidized by the action of a chlorate or a soluble chromate, producing a very beautiful and very fast black.

In order to produce a black in paste or dry powder, suitable for employment, either for printing on stuffs, and fixing with albumen or any other size, or for the fabrication of colors, for varnishes and inks, I operate thus:

Into a solution of a per-salt of iron or copper I pour aniline oil, and then a solution of a chlorate or soluble chromate.

REMARKS ON GRAWITZ'S PATENT,

No. 105130.

1st. The method of producing black by the action of a chlorate on the pretented chloride of iron-aniline (a mixture of hydrochloride of aniline and basic perchloride of iron) is borrowed from Higgin's second patent (p. 48). According to Kruis, per-salts of iron react on a mixture of hydrochloride of aniline and of chlorate of potash, giving a black. Therefore there is nothing new here.

2d. The action of a chromate on the pretented iron-aniline is included in the processes of Perkin (p. 16), Kopp (pp. 9-16), Bobœuf (pp. 54-58), Glanzmann (pp. 21-23).

3d. The action of a chlorate on a salt of copper-aniline does not give a black in the cold, and badly with heat.

4th. As to the action of a chromate on a salt of copper-aniline, we make the same observation as under 2d, and we again mention the experiments of Dale and Caro (p. 17). The chloride of copper-aniline is, moreover, very easily decomposed alone, giving a black mass (Schiff, p. 87).

Of these four processes the first and second only give a black practically.

The four mixtures, on the contrary, give a black easily if an acid be added, or instead of aniline oil a neutral aniline salt be taken. Grawitz, at the close of his patent, also claims this last method of operating, but in this case he only claims what all the world had given him.

The best proportions are those which correspond to aniline, the iron or copper salt, and the chlorate or soluble chromate, in proportion to their chemical equivalents.

I allow the reaction to proceed in the cold for some hours, or excite the action by heat. A black precipitate is formed, which I collect and wash on a filter.

This black precipitate in paste, having great covering properties, is eminently suitable for the printing of fabrics of all kinds, the color being fixed with the aid of albumen or any other analogous material.

In this manner aniline black may be associated with all other colors in printing.

REMARKS ON GRAWITZ'S PATENT, NO. 105130.

The employment of aniline, in place of its salts, and particularly in place of its salts in presence of acids, was a modification, a retrograde improvement on known processes; if, however, the operation goes on, it is on account of the formation of a salt of aniline during the reaction.

Are such modifications of simple and known processes by less practicable processes patentable?

We think not. In any case, the holding of a parallel patent does not evidently confer the right to exclude others already public property.

The phrase relating to chemical equivalents appears to be introduced by the author solely to give a scientific aspect to his patent in the eyes of those unfamiliar with chemistry. No chemist would take it seriously. An equivalent of chlorate, ($KO\ Cl\ O_5$), gives up when acting as an oxidant, 6 equivalents of oxygen; 1 equivalent of bichromate, $KO(CrO_3)_2$, gives up three; and one equivalent of neutral chromate, $KO\ Cr\ O_3$, one and one-half. And equal equivalents of these three bodies have the same oxidizing action of the "metal-aniline"!

It seems to us an incredible fact that some scientific chemists, like the experts of Douai, should allow themselves to take seriously a mere phantasmagoria of words, which do not merit discussion, and have been able to consider it a patentable novelty.

We will say, in passing, that it has been demonstrated in practice that in order to oxidize *one* equivalent of aniline to the state of black, it is necessary to employ two-fifths to one-half an equivalent of chlorate and about *one* equivalent of bichromate, being, in these two cases, between two and three equivalents of oxygen.

GRAWITZ'S PATENT, NO. 105130.

To produce aniline black on fabrics, which may be either silk, wool, thread or cotton, I proceed in two distinct manners.

1st. I print, by means of convenient thickening, a mixture of the three reagents indicated, aniline, a per-salt of copper or iron, and a chlorate or soluble chromate. The color develops rapidly on exposure. It appears in all its beauty after washing and scouring.

2d. I print of the fabric with a salt of metal-aniline, and then pass it through a bath of a chlorate or soluble chromate. I can also print with a mixture of aniline and a chlorate or soluble chromate, and pass into a bath of a per-salt of iron or copper.

The principal advantages of my process, aside from the yield, which is enormous, are the following:

1st. The economy. This is evident.

2d. The absence of all free acid, which is capable of attacking the metallic portions with which the pieces come in contact.

3d. The possible absence of all traces of copper, which can be deposited on the steel doctors and rollers.

I claim, therefore, as my exclusive property, during five years, the right to fabricate prepared aniline black to be put upon fabrics, by one of the two following processes, in such a manner as it may be thus applied.

Mutual reaction of aniline oil on a per-salt of iron or copper, or of a soluble chlorate.

REMARKS ON GRAWITZ'S PATENT, NO. 105130.

The first process : aniline, salt of copper or iron, and chlorate, is only Lightfoot's process as modified by the colorists (pp. 42–46), or that of Higgin of 1867 (p. 48) ; the second, aniline, salt of copper or iron, and chromate is *utterly worthless*, as the author subsequently found by experiment—probably after the issue—of the process he had patented at random (see the first *certificat d'addition.*)

The various processes enumerated under rubric No. 2, lack common sense ; no colorist would wish to take the trouble to try them ?

In conclusion what does this patent contain ? Some formulas for the preparation of black in powder, containing the known elements, but modifying old processes so as to render them impracticable or disadvantageous.

A process for printing copied from Lightfoot and Higgin, and a series of others, in which known agents are employed, under conditions where they practically give nothing.

This patent, therefore appears to us absolutely reduced to a nullity, and we do not comprehend why it has not been annulled for a long time by the courts.

Note that this patent is exclusively devoted to printing and to powders. This remark is not unnecessary, as it appears that Grawitz, nevertheless reverts to it as the basis of his actions for infringement against dyers.

GRAWITZ'S PATENT, NO. 105130.

Mutual reaction of aniline oil, of a per-salt of iron or copper, and of a soluble chromate.

The following recipes are extremely economical :

Sulphate of copper, bichromate of potash, aniline oil ;

Sulphate of peroxide of iron, bichromate of potash, aniline oil ;

In place of aniline oil, a neutral aniline salt may be employed, this constitutes an important improvement on the processes actually used, in which an acid is added which augments the cost and does not improve the product, I, nevertheless, claim it.

All of these processes and applications, I claim by the present patent, as my property for five years.

CERTIFICAT D'ADDITION TO PATENT NO. 105130

OF OCTOBER 3, 1874.

When it was desired to produce of the fabrics themselves (whatever be their nature, silk, wool, thread or cotton), my aniline black, which results from the concomitant action on aniline or its salts on bichromate of potash (and more generally of a soluble chromate, and of per-salts of iron and copper, it is produced with the usual thickening of starch, so that the color develops very badly and very slowly.

The development is much more rapid with the salts of aniline than with aniline oil, and still more with the salts of aniline and any acid.

I therefore modify my process in the following manner :

For black in paste and in powder there is no necessity of a change. The production of black is rendered more rapid and much easier with the salts of aniline, and still more with the salts and an excess of acid.

I claim, therefore, the preparation in this sense :

In order to make the black develop on fabrics, I print with the aid of thickening :

1st. A salt of aniline, per-salt or iron or copper, and bichromate of potash, or in general a soluble chromate, and expose to the air.

Or as well :

2d. I print the preceding mixture with excess of acid.

Or as well :

3d. I print a salt of aniline, and a per-salt of iron or copper, and I pass through a bath of bichromate of potash or a soluble chromate with excess of free acids.

REMARKS ON THIS CERTIFICAT D'ADDITION.

Three days after taking out his first patent, Grawitz, having without doubt judged it wise in the interval, to submit to experiment the reactions he had patented, himself perceived that " his aniline black," which resulted from the action of the salts of iron and copper and bichromate of potash on aniline, developed badly. In the first patent he had said that the color developed rapidly on exposure.

It is to be remarked that he designated the black in question as " his black." It seems to us, however, that the black had already been obtained by many other manufacturers. It is true, that these had been prepared with salts of aniline and excess of acid. Grawitz had modified the process in suppressing the acid ; he again returned to the acid, that is to say, to the process of his predecessors which he had perfected backwards.

He did not refrain from speaking of " his black," and claiming the process thus modified, that is to say, process which had long been found as public property or in anterior patents.

The first and second processes for printing could have only been proposed by a man absolutely ignorant of that art.

According to the first process, the color develops badly and, moreover, can not be preserved in the mixture ; according to the second, it developeds in the mixture, itself but not on the fabric.

If the author had taken the pains to experiment with his processes thoroughly before patenting them he

CERTIFICAT D'ADDITION TO PATENT NO. 105120, OF OCTOBER 3, 1874.

I also claim, by the present "certificat," the right of applying to the dyeing of fabrics or threads of silk, wool, thread or cotton, my aniline black, resulting from the *concomitant* action *on aniline or its salts of per-salts of iron or copper and of soluble chromates or bichromates.*

To dye, I pass the threads or fabrics through a bath formed of a mixture of salts of aniline and of per-salts of iron or copper.

I then pass into a bath containing soluble chromates or bichromates and excess of acid.

In all these operations, the blacks produced vary in shade, according to the acid combined, as well as the aniline, the iron or the copper, or according to the chromate bath, from blue-black to maroon-black, and passing to violet-black and black.

would not have exposed himself to become the laughing-stock of colorists.

The processes No. 3, are no longer practiced. Besides, they are contained in previously published experiments, thanks to Lightfoot, C. Kœchlin, Lauth, and others, who had at the same time elaborated practicable and simple methods, methods still in use at present, after twenty years, without modification.

All of the first part of the *certificat d'addition* which refers to blacks in powder and for printing, is also null, like the principal patent, inasmuch as there is no question of dyeing.

We will now look at the dyeing part. What do we find there? The formation of black on the fibre:

1st. By passing the fibre through a bath containing an aniline salt, and a per-salt of iron, or

2d. A salt of aniline and per-salt of copper, and subsequent oxidation in a chromate bath containing excess of acid.

Kopp had pointed out (p. 13), that by impregnating the fibre with a per-salt of iron and salt of aniline, emeraldine is formed, and Wood and Wright (p. 41), and also others after them, had oxidized emeraldine to black by a passage through bichromate.

Does this combination of two known processes, to obtain a result equally well-known, constitute a patentable novelty?

Jarosson and Mueller-Pack (p. 67) obtained the identical black of Grawitz (resulting from the concomitant action), by mordanting the fibres in proto-salts of iron, allowing to oxidize in the air, passing into an aniline salt and then through bichromate.

Wood and Wright had also formed emeraldine on

the fibre by the action of nitrate of copper on a salt of aniline, subsequently having oxidized it by bichromate.

In what respect does this second process of Grawitz show the stamp of novelty.

Note again, that with the *salts of aniline* and the salts of copper, *copper-aniline* combinations are not formed, but only double salts.

It seems to us after this, that as far as dyeing is concerned, the *certificat d'addition* is, as well as the principal patent, is forfeitable.

From a judicial point of view, if a patent is declared null, the *certificat d' addition* is annulled with it; but we will not detain ourselves with this consideration. It seems to us interesting to demonstrate that the *certificats d'addition* which Grawitz has registered on his principal patent, are themselves worthless as being nullities, independent of any other consideration.)

GRAWITZ'S PATENT OF NOV. 3 1874.

No. 105554.

The object of the present patent is, to reserve to myself the exclusive right of dyeing in black, or in shades approximate to black, such as maroon, blue-black, or violet-black, with aniline, all textile materials of whatsoever nature they may be, in the raw state, as threads, or fabrics.

The color is developed by the concomitant action on aniline oil, or on its salts, by the following reagents:

1st. Chromates or bichromates or soluble chlorates,

2d. Salts of iron, of copper, of manganese, of nickel, of cobalt, or others at their highest degree of oxidation. The proto-salts may also be employed, for they also pass by the same process into salts of the sesquioxide, but the shades are less beautiful.

REMARKS ON GRAWITZ'S PATENT OF NOV. 3, 1874,

No. 105554.

The exclusive right to dye with aniline black. Excuse us a minute! Why does not Grawitz claim at the same time the monopoly of dyeing with all other colors with raw materials arising from all other sources?

He had an equal right to all of them.

The concomitant action exercised on aniline by the bichromates and chlorates, or by the salts of iron, of copper, of manganese, of nickel, of cobalt and OTHERS, at their highest degree of oxidation.

It is in part a repetition of the claims of patent No. 105130, which the author himself had already seen to be a nullity; he, therefore, here endeavors to save himself by a complication. He claims, in effect, the blacks produced by:

1st. Per-salts of iron and chromate.
2d. Per-salts of copper and chromate.
3d. Per-salts of manganese and chromate.
4th. Per-salts of nickel and chromate.
5th. Per-salts of cobalt and chromate.
6th. Per-salts of iron and chlorate.
7th. Per-salts of copper and chlorate.
8th. Per-salts of manganese and chlorate.
9th. Per-salts of nickel and chlorate.
10th. Per-salts of cobalt and chlorate.
11th. Other (per-salts) with chromate and chlorate.

By permutation and combination of the various reagents, two to two, three to three, or four to four, one

The nature of the black I produce, is very probably a black of a metal-aniline. One molecule of hydrogen in the aniline is replaced by a metallic molecule, and that complex base is oxidized by the soluble bichromates, or the chlorates.

arrives at a very respectable number of possibilities, of which we can dispose without question or discussion.

1st. Included in Persoz's process (p. 9, note 4), Kopp (p. 13), and with the subsequent oxidation by chromate, Jarosson and Mueller-Pack (p. 67), etc.

2d. In the processes of Wood and Wright (p. 41).

3d. 4th and 5th, appear to us to belong properly to Grawitz, but he omitted to tell how he prepared *industrially* the per-salts of manganese, nickel and cobalt.

6th. Is of Wood, Wright, and others.

7th. Lightfoot.

9th. Pinckney, if the proto-salts of nickel are used, the per-salts belong to Grawitz.

To the 8th and 10th, the same observation applies, as to the 3d, 4th and 5th.

11th. And others! It is difficult to discuss a claim formulated in a manner so precise.

Here we again return to the metal-aniline. That is in the state of black. He will be very accommodating if he will tell us what he means by that. If he wishes to say, that in producing black on the fabrics, a metallic oxide is fixed at the same time, he tells us nothing new; all the world knows that, or does so without knowing it, as M. Jourdain makes his prose.

Nothing was known in regard to the chemical nature of aniline black in 1874, and it is not known much more exactly now.

In order to accomplish the reaction, I operate in two different manners.

I then dip the textile fibres in aniline oil, allow to drain, then pass into a solution of a metallic salt, which immediately forms a precipitate fixed on the fibre, containing aniline and metal. Then I pass to a bath of a soluble bichromate, acid or not.

The process is delicate in its application.

The following is better:

A bath is formed containing salts of aniline and copper, mordanting the fibres in the bath, and oxidizing in soluble chromates or bichromates or even chlorates.

It is best to have the double metallic and aniline salts well combined, for example, when iron is used, the ferrocyanides and ferricyanides of aniline.

The following proportions give good results. I reserve to myself the variation of them:

For cotton, and for hemp and linen thread:

One litre water.

125 grams hydrochloride of aniline.

85 " bichloride of copper.

50 " nitrate of sesquioxide of iron.

Allow the material to become saturated in the bath, then pass into a bichromate solution, then having well drained and wrung out, rinse, as needed.

The bichromate bath gives the best results for black

It seems, however, that the strongly oxidized blacks which contain oxygen, form with metallic oxides, true lakes, but if this is it, it was not Grawitz who discovered them.[1] He has the talent—we will not dispute him that—to find a pretty name, so as to give his lucubrations a scientific tint, and by this means has known how to impose well on some persons, depending for the most part, at least, on their credulity.

It is a beautiful thing to know how to express it !

This first method appears well and proper in Grawitz. No person before him had the idea of proposing such a ridiculous process. The author also himself qualifies it as delicate. He also finds it to be *economical.* (In his first patent he said, the *economy* of the process is *evident.*)

The second process has nothing new in principle. Blacks had been produced by the action of bichromate on emeraldine formed by the salts of iron or salts of copper. Grawitz produced it by the two together, following by chromate.—Combining two known processes to obtain a known result.

Under pretext of "aniline salts," Grawitz attempts to include in his patent Cordillot's ferricyanide process. From a practical point of view, we do not see any good that he has accomplished, except having borrowed so much from the processes of others, he doubtless thought that he could not fail to make Cordillot contribute also.

The processes for dyeing wool and other animal matters are not new and present no interest. What remains of this patent? Nothing, in all these cases, nothing practical. It seems to us, therefore, that it also should be annulled.

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[1] See on this subject Glanzmann, p. 21.

when cold and dilute. For cotton, it may be very slightly acidified with organic or mineral acids in the proportions necessary to saturate the alkali of the bichromate, or even to hold in solution all of the oxide of chromium arising from its reduction. This is the best procedure, but is not peremptory.

For dying wool, silk, hair, and feathers, it is preferable to begin by dying the silk, wool, etc., in nitric acid, then yellow in chromic acid, then operate as above, except that acid salts of aniline and metal may be taken, and the chromate bath acidified more strongly, without fear of attacking the fibres.

There is thus obtained, according to the nature of the acids entering into the composition of the different salts, shades from maroon even to blue, and passing to violet and black.

When very black shades are desired, attention must be given to the purity of the aniline.

Such is the *ensemble* of processes and applications, which I reserve for five years by the present patent.

The order of the passages through the bath may be inverted.

CERTIFICAT D'ADDITION TO PATENT

No. 105130, OF APRIL 29, 1875.

In my present demand for a certificat d'addition to my patent of September 30, 1874, I proceed to describe my new method for the production of black or of shades approximating to black, by the concurrent reaction on aniline oil or its salts, of certain metallic salts and of chromates and bichromates.

The salts suitable for giving a black are the salts of the following metals:

Iron, copper, manganese, cerium, aluminium, chromium, nickel, cobalt, tungsten, vanadium, lead, etc., in general all the metals capable of presenting two degrees of oxidation susceptible of being transformed into each other. For example, iron, of which the salts of the protoxide are changed into the sesquioxide by the fixation of oxygen, and of which the salts of the sesquioxide are transformed into those of the protoxide by reducing influences.

REMARKS ON THE CERTIFICAT D'ADDITION TO PATENT NO. 105130,

OF APRIL 29, 1886.

If Grawitz had described properly "his method" the first time, or if he had described it all, he would not have had to describe it again.

We will now compare the method of September 30, 1874, with that of April 29, 1875, and find that they do not resemble each other at all. The originality of the first was to work with aniline oil, and not to employ an acid, and in the novelty described by Grawitz he changes this totally, and recommends on the contrary the employment of the acid in excess.

The metals of two degrees of oxidation which intervene here, now become more numerous. We are not told that they are always employed with aniline in proportion to their chemical equivalents. We must suppose so, since it is so, according to Grawitz, in the original lines of his first patent. The process, therefore, becomes above all, one of "evident economy" in the case of vanadium.

Among the metals of many degrees of oxidation we we find *aluminium* included. This fact is extremely interesting, and it is deeply to be regretted that Grawitz has published nothing in regard to the two degrees of oxidation of this metal.

Since according to these patents it ought to have them, ought not he to claim for his own such a remarkable discovery.

The per-salts of lead are also very interesting.

CERTIFICAT D'ADDITION TO PATENT NO. 105180 OF APRIL 29, 1875.

To apply this reaction, I proceed in two distinct manners:

1st. Production of black in paste or in dry powder, insoluble in the reagents, suitable for the printing of stuffs or of papers, and the fabrication of colors, varnishes and inks of all kinds.

2d. Production of black on the textile fabrics themselves.

1ST. PRODUCTION OF BLACK IN PASTE OR IN DRY POWDER.

This is the best manner of operating:

I pour in a solution of a per-salt of iron, for example, sufficient oil of aniline to produce a precipitate. Then I pour into the semi-fluid mass which is produced, a solution of bichromate of potash. It forms a precipitate, which I wash on the filter or by decantation, at first with pure water, then alkaline water, in order to destroy the greenish reflex.

The total quantity of acid added ought to suffice to neutralize the bichromate of potash, and the oxide of chromium proceeding from the reduction of the chromic acid.

The reaction is intensified by elevation of temperature.

2D. PRODUCTION OF BLACK ON THE FIBRES THEMSELVES BY PRINTING.

I operate in one of the three following ways:

REMARKS ON THE CERTIFCAT D'ADDITION TO PATENT NO. 105180 OF APRIL 29, 1875.

In concluding this theoretical introduction, is it not an echo of the old theory of the generation of black by the alternate reduction and reoxidation of the salts of copper, a theory, which, as we have shown, was victoriously refuted by Rosenstiehl.

By working thus, hydrated peroxide of iron and hydrochloride of aniline are obtained. It takes *three* equivalents of hydrochloride of aniline to *one* equivalent of perchloride of iron. The hydrochloride of aniline is then oxidized by the acid bichromate. The quantities of acid indicated are *four* equivalents to *one* bichromate.

$$K\,O\,(Cr\,O_3)_2 + 4\,H\,Cl = K\,Cl + Cr_2\,Cl_3 + 4\,HO + O_3$$

CERTIFICAT D'ADDITION TO PATENT NO. 105180 OF APRIL 29, 1875.

1st. I print with the aid of suitable thickening, starch, gum-tragacanth, or others, a mixture of: 1st, a salt of aniline, 2d, a metallic salt of the metals above indicated, 3d, bichromate or soluble chromate. I develop the color by exposure;

2d. I print a mixture of a salt of aniline with an organic acid, and an easily decomposable metallic chromate, and then steam.

3d. I print a mixture of a salt of aniline, and a metallic salt of the metals indicated above, and pass into a dilute neutral solution, or better an acid solution, of a soluble chromate or bichromate.

The proportion of the aniline in the mixture varies from 5 to 10%.

The best relative proportions of aniline, of the metalic salt, and of chromate or bichromate, ought to be those of their chemical equivalents.

In order to dye textile materials with aniline black, a salt of iron, for example, is employed as follows:

I form a bath A, containing for 100 litres:

Hydrocloric acid of 10°–20° Bé.....	8 litres
Aniline oil.....	4 "
Liquid perchloride of iron of 45° Bé.	4 "

The rest water.

I also form a second bath, B, containing:

Water.....	1000 litres
Bichromate of potash.....?	8 kilos.

I first mordant the textile materials in bath A, draining and expressing with care the excess of liquid which I collect, then I allow the materials thus mordanted to digest for five or six hours in the second bath B.

REMARKS ON THE CERTIFICAT D'ADDITION TO PATENT NO. 105180 OF APRIL 29, 1875.

The first process for printing is worthless, as presenting nothing new in the way of a reaction.

2d. The second is no longer practicable; if a soluble chromate be taken, the color develops in the thickening, if an insoluble chromate be taken it does not develop at all.

This is the process of Alfred Paraf, omitting the chlorate, perfected backwards by Grawitz, as is his habit.

3d. The same operation here as to 1st.

The printers, who have perfected Lightfoot's process have very naturally been experimenting with the inventions of Grawitz; but he has never dreamed of doing so.

The process for dyeing is only that of Kopp, with the bichromate development of Wood and Wright, and also that of Jarosson and Mueller-Pack, using two baths.

Grawitz is behind them about five years.

CERTIFICAT D'ADDITION TO PATENT 105130 OF APRIL 29, 1875.

The bath B is sufficient to develop the color on 200 kilos of cotton, for example.

I then wash the cotton, on removal from bath B, with cold water, wring out the water, and recommence the same series of operations, that is to say:

1st. Mordanting in the bath A.

2d. Digestion in the bath B; and thus in succession, until a sufficiently dark shade is obtained.

The end of the operation is reached, when the material to be dyed, perfectly washed on taking from the chromate bath with cold and then with hot water, presents a brown reflex.

At this moment, after perfect washing with boiling water, on passing the cotton through a boiling soap bath containing about 10 grains per litre, it changes its shade to a bluish black. Carbonate of soda gives a violet shade.

For piece-goods, the mordanting may be done while folded, and the color developed by passing the pieces loosely through a vat with rollers, or other suitable apparatus.

The rapidity of the development of the color is accelerated by the *greater concentration of the liquors and especially by their degree of acidity.*

In dyeing cotton, attention should be given to employ nothing to weaken the fibre.

The bath of chromate may be replaced by a bath of chlorate, but it is dearer and the shades less good; I however reserve its employment.

I dye in this manner cotton, linen, hemp, wool, silk, feathers, skins, hair, wood, and in general, all materials susceptible of being dyed.

REMARKS ON THE CERTIFICAT D'ADDITION TO PATENT NO. 105180 OF APRIL 29, 1875.

CERTIFICAT D'ADDITION TO PATENT NO. 105180 OF APRIL 29, 1875.

In conclusion, I claim, therefore, the production of black by the concurrent action on aniline oil or its salts of certain metallic salts, and a solution of soluble chromates or bichromates. I also claim the right to apply these reactions, not only with pure aniline which gives the black, but also with commercial anilines which give shades approaching to black, toluidine which gives a brown, naphtylamine which gives a puce, and bases derived from aniline by substitution, such, for example, as ethylaniline, methylaniline, diphenylamine, etc.

Such is the *ensemble* of reaction, products and applications, which I claim by the present "*certificat d'addition.*"

REMARKS ON THE CERTIFICAT D'ADDITION TO PATENT NO. 105130 OF APRIL 29, 1875.

The final claims of Grawitz are reproductions from his predecessors, and not very sharp, but rather foolish, so that we do not think it necessary to give a list of them this time.

The reader is urged to compare with the general introduction.

We, therefore, think that the second *certificat d'addition* resembles the first, as well as the principal patent, in its character.

CERTIFICAT D'ADDITION TO PATENT

No. 105554, OF AUG. 24, 1876.

The object of the present certificat d'addition is to recapitulate the chemical reactions which I have patented for the application of aniline to the production of black, or of shades approaching to black; also the processes which I have reserved to myself, and which I shall now reserve to myself, for use in the dyeing of textile materials.

By my principal patent of Sept. 30, 1874, perfected on Nov. 3 of the same year, and by the *certificats d'addition* thereto attached, I have intended to patent and claim three things:

1st. A series of chemical reactions giving, with aniline, black or shades approaching black.

2d. A series of processes for the utilization of these reactions.

3d. The application of this *ensemble* of processes and reactions to the dyeing of textile materials of all kinds, and the claim to the exclusive right of dyeing with aniline, black or shades approaching to black, on materials of animal origin, a result absolutely new and patentable in itself, independent of any process.

REMARKS ON THE CERTIFICAT D'ADDITION TO PATENT 105554

OF AUGUST 24, 1876.

Grawitz decidedly loves recapitulations.

It is a convenient process, to pass over in silence that which he knows to be impracticable and of little use, and to accumulate on the same occasion in his patents, all the progress meanwhile realized by others.

1st.—These chemical reactions have nothing new in themselves. In some cases he has chosen to carry them out under less favorable conditions than his predecessors; and in this all the novelty consists.

2d.—The processes, in so far as they are applicable, are no longer new. He has, it is true, indicated a certain number of novelties, but they are distinguished by their absurdity, and no person will contest their paternity with him. But these processes have evidently not been applied, for they are not applicable.

3d.—Grawitz has by no means the right to reserve to himself known processes and reactions to the dyeing of all kinds of textile materials, as long before his time, aniline black was made on cotton by printing as well as by dyeing. As regards his pretence to reserve the dyeing with aniline of black and shades approaching to

CERTIFICAT D'ADDITION TO PATENT NO. 105554 OF AUGUST 24, 1876.

The *ensemble* of chemical reactions, of which I have patented the application to the production of black, resulting from the concomitant action on aniline oil or its salts, of certain metallic salts and soluble chromates or bichromates, or even chlorates, *without exposure to air.*

I have indicated and patented three principal methods for applying these reactions.

The first consist in the formation of a complex base containing at the same time aniline and a metal, a complex base which has been obtained by precipitating certain metallic salts with aniline oil. These complex bases redissolve in acids.

The second method, is the formation of a bath containing a double salt of aniline and a metal. For example: equal equivalents of perchloride of iron and hydrochloride of aniline are placed in the bath.

The third consists in the formation of a bath containing the elements of an aniline salt, combined with a metal, that is to say, the aniline salt of a metallic acid.

black on animal materials, it is absolutely ridiculous after the patents of Persoz (p. 62), Gonin and Glanzmann, the publications of Reimann (p. 63), and others. Grawitz ignores or affects to ignore these authorities.

The exposure to air, to which he here attaches much importance, is in no wise essential to the production of black. The modified Lightfoot black may be developed, without exposure, by steaming for 1 or 2 minutes.

The older processes of dyeing (Bobœuf, Alland, Paraf-Javal, Persoz, Lauth, and others) do not employ this exposure.

As to Jarosson and Mueller-Pack, they finish the oxidation of the black in closed vat; it seems to us not exactly an *exposure* but a *screening from the air*. The manganese blacks of Lauth are also developed without exposure.

The complex bases! Grawitz obtained with the salts of copper and aniline the salts of phenyl-cupramonium, known long before him. In redissolving these salts in an acid there may be formed, either double salts, or a simple mixture of the aniline and the copper salt.

In all this, he only tries to throw dust in the eyes of such persons as do not examine to closely.

The second method contains no novelty as we have repeatedly shown. The perchloride of iron and hydrochloride of aniline do not form a double salt, even if we must offend Grawitz.

The third method, that of a single bath, or *plain bath*, containing all the elements necessary to produce black, he has *never* spoken off.

It is found in the patents of Bobœuf, Paraf-Javal, and Persoz, but he has doubtless never seen it, or he would not have omitted to appropriate it immediately. It

CERTIFICAT D'ADDITION TO PATENT NO. 105554 OF AUGUST 24, 1876.

This last method comprehends the formation by double decomposition in the baths of ferro and ferricyanide of aniline, of chromates and bichromates, of manganates and permanganates, of tungstates, vanadates and bivanadates of aniline. These complex bases, these double salts of aniline and of metal, these aniline salts of a metallic acid, have the property of allowing the aniline to oxidize progressively with the greatest facility, and produce black, or shades approaching black, if the oxidation has not progressed for a sufficient time.

In order to apply this *ensemble* of reactions and processes to the dyeing of textile materials, the operating may be effected in two or three dips, or at a single dip, and in two or three baths or a single bath.

may be necessary for Pinckney, Coquillion and Jeannolle to call his attention to it.

As to the phraseology of Grawitz, it is distinguished by an evidently calculated obscurity.

According to him, the third method consists "in the formation of a bath containing the elements of an aniline salt combined with a metal." (We do not comprehend at all what he wishes to say, and we will wager he does not comprehend himself), but the phrase sounds well and this is his intention, as also in the phrase "aniline salts of a metallic acid." This we comprehend very well, so well that we see clearly *why Grawitz has not spoken before of it.* He had mentioned the salts of metal-aniline, the double salts of aniline and a metal, but never of the aniline salts of a metallic acid. He had insufficiently studied his Bobœuf, and was evidently in doubt about the existence of bichromate of aniline.

"This last method, etc." In these four lines he reveals some things well. The manganates and permanganates of aniline! Has Grawitz seen them? He is more happy than most chemists, among whom not only *permanganic acid* but *permanganate of potash* immediately oxidizes aniline in place of forming a salt.

These complex bases (which do not exist), these double salts of aniline and metal (which will not be questioned), these aniline salts of a metallic acid (here we have them at last) allow, etc. This has been known for a long time, from Fritzche, from Perkin, from Bobœuf.

CERTIFICAT D'ADDITION TO PATENT NO. 105554 OF AUGUST 24, 1876.

The manner of dyeing in three baths is as follows :

The complex bases of which I have spoken are precipitated on the material to be dyed, by passing the materials of whatever nature into aniline, then into a metallic salt, draining carefully between the two baths. The black is then developed, by passing the material through a bath of chromates, bichromates, or even soluble chlorates.

For operating into two baths there are two distinct manners :

Allow the materials to become saturated in a closed bath, which may be ; 1st, the elements of a double salt of aniline and a metal ; or, 2d, the aniline salt of a metallic acid. The materials become dyed a green, becoming darker and darker, in this bath, in the cold, or better with heat. These are true colors, for they can be rinsed with impunity. The aniline is then peroxidized and the black developed by taking the materials to be dyed to a bath of chromate, bichromate, or even a soluble chlorate.

To dye in the same bath, it may be effected in two ways :

Allow the materials in the bath containing only the metallic elements and aniline to there acquire gradually a darker green color, then add to the same bath the peroxidant, a chlorate, or a soluble chromate or bichromate.

On the other hand, all of the elements necessary to produce the black may be added at once to the bath, in such a state of concentration that they will not be precipitated immediately, but will commence to react promptly on the introduction of the material to be dyed, either at ordinary temperatures, which is best when chromates and bichromates are employed, or at an

REMARKS ON THE CERTIFICAT D'ADDITION TO PATENT NO. 105554 OF AUGUST 24, 1876.

The dyeing in three baths, practised at the hands of Jarosson and Mueller-Pack, is with Grawitz (in one of its forms, passing through aniline and then a metallic salt) as absurd on August 24, 1876, as October 3, 1874.

The method in two baths is applicable but is not new.

Grawitz loves to revert continually to the same arguments; we will abstain from following him in this course, and refer the reader to our previous revelations.

This is all Bobœuf. Paraf-Javal and Persoz also proposed this method of operating.

elevated temperature, which is best in employing chlorates.

This last manner of operating; by adding all at once to the dye-bath all of its constituent elements, effects an enormous improvement in dyeing, especially of piece goods.

The aniline salts of metallic acids which give the most remarkable results are those where the metallic acid is chromic acid.

In a bath containing by a double decomposition the elements of chromate of aniline without excess of chromic acid, the tissues only darken to the extent of a dark green, becoming violet-blue by passage through an alkali, exactly as with the chloride or nitrate of the sesquioxide of iron.

If it be peroxidized by a passage through a soluble bichromate or chromate, this green gives the black. The bath should contain a sufficient quantity of bichromate or chromate to develop the black at one dip. When a chlorate is used, tke quantity of acid in the bath should suffice to saturate the base combined with the chloric acid.

When chromates and bichromates are employed, not only the base combined with the chromic acid should be saturated, but also the oxide of chromium arising from the reduction of the chromic acid.

The metals, the salts of which give one or another of the reactions indicated, are those metals presenting two degrees of oxidation, easily convertible into each other by oxidation and reduction, and especially the following of which the energy is very great: iron, copper, manganese, cerium, chromium, nickel, cobalt, tungsten and vanadium.

REMARKS ON THE CERTIFICAT D'ADDITION OF PATENT NO. 105554 OF AUG. 24, 1876.

It is not Grawitz who realized this "enormous" improvement. Bobœuf, Paraf-Javal, and Persoz had indicated it, and all "skillful and intelligent" dyers had the right to use their processes. The patents of Coquillion and Jeannolle were necessary to reveal to Grawitz the advantages of the single bath.

See again, Bobœuff and others.

The neutral chromate Grawitz here specifies does not exist. It is not sufficient to take the bichromate, but the bichromate in presence of acid is necessary, as Bobœuf and others had clearly indicated.

Here Grawitz himself indicates the necessity of the acid.

CERTIFICAT D'ADDITION TO PATENT NO. 105554 OF AUGUST 24, 1876.

I reserve to myself the use of all these mineral or organic acids, whether combined with metals or with aniline, the same being free in the dye-baths, so as to enter into the preceding reactions. The shades obtained vary with these acids.

The processes I have indicated may be combined among themselves, so as to obtain an infinity of proportions for the dye-bath, but the black will only result by means of the reactions which I have patented, and of which I have reserved to myself the application in such a manner as to be utilizable.

I give two examples of dyeing for 100 kilos. cotton. I take :

Water	800	litres
Bichloride of copper	250	grams
Aniline oil	6	kilos
Hydrochloric acid	24	"
Bichromate of potash	9	" 600 grams.

I enter the materials at the ordinary temperature, and at the commencement work them frequently in the bath, then more slowly. The dyeing is completed in one hour or even less. The black shows a bronze reflex which is removed by boiling with soap. The copper may be omitted.

Second example :

Water	100	litres.
Aniline Oil	6	kilos.
Hydrochloric Acid of 19° Bé.	12	"
Chlorate of Potash	8	"
Perchloride of Iron of 50° Bé.	8	"

I mix cold or lukewarm and gradually raise the temperature. Then I wash and soap.

For pieces-goods, they may be operated in the vat on rollers or other appropriate apparatus.

REMARKS ON THE CERTIFICAT D'ADDITION TO PATENT NO. 105554 OF AUGUST 24, 1876.

Always the same habit of claiming for himself what is common property (see Bobœuf).

The impudence, the impudence, the monstrous impudence! Unless he takes care he will go altogether beyond the limits of license. All the world has not been able to study the question profoundly, and to appreciate the trenchant and haughty manner of Grawitz, but will hardly be able to believe *a priori* in all that he claims; it amounts to nothing, absolutely nothing, but some impracticable process, and some theoretical speculations unworthy even of an alchemist.

The copper may be omitted. That little phrase is worth in itself a long poem. If there is to be no longer chloride of copper to form the metal-aniline, what becomes of the "concurrent and concomitant" action. There is no longer the "catalytic action" of happy memory, on which Grawitz has also drawn so extensively.

Alas! alas! we see Bobœuf in this, and nothing else.

CERTIFICAT D'ADDITION TO PATENT NO. 105554 OF AUGUST 24, 1876.

Chlorates give less desirable shades of black than chromates.

For certain shades, chromates and chlorates may be combined at the same time for blacks. When chromates are in the bath, the conducting of the operation with heating becomes very delicate; it is better to proceed at the ordinary temperature.

I will remark in conclusion, that my blacks from chromates differ radically from the blacks of Lightfoot in the elements entering into their production, and my chlorate blacks in their development which does not require exposure. I am the first to have found and applied to development on the textile fibres themselves, these green and black precipitates which are formed in the baths. With convenient proportions the baths remain limpid and all the precipitate is formed in the fibres. My blacks from chromates are evidently the same that Perkin produced together with his violet, and of which he did not perceive the importance in 1859, four years before Lightfoot's patent, blacks which have never since been successfully fixed on the fibres. Such is altogether, the reactions, the processes, and applications, which constitute my property, by virtue of my different patents and *certificats d'addition.*

It is unnecessary to add that I can give a charge of aniline per kilo. to the textile material, proportionate to the intensity of the black it is desired to obtain. I have indicated the proportions of black preferable for medium shades. When the proportion of aniline is very small,

REMARKS ON THE CERTIFICAT D'ADDITION OF PATENT NO. 105554 OF AUGUST 24, 1876.

The processes with chlorates are of no practical value; they are expensive, they give inferior blacks to the chromate process; this is Woods and Wright in a single bath without exposure, it is Coquillion almost literally.

Therefore, on August 24, 1876, Grawitz did not yet know how to dye with chromates and heat. Although having the documents containing the experiments of others at hand, he has not had the honor to possess intelligence enough for a dyer.

This is absolutely incorrect.

Perkin's black had been employed as a color with albumen. (See p. 19.)

Bobœuf had produced the same on the fibre, Alland, Paraf-Javal, Persoz, etc., had done the same, either in one or many baths.

This assemblage does not constitute the sole property of Grawitz; it is public property, as Grawitz vainly tries to dispute.

The chemical equivalents, the discovery dear to the heart of Grawitz; it is a long time since he has spoken of that!

This *certificat d'addition*, we are happy to state, is the work of a very skillful casuist. Under pretext of recapitulation, Grawitz claims many practical processes belonging to others or public property; by his own assurance he tries to frighten the timid.

This is a patent of monopoly of the first class; it is

it is better to use less water and increase the quantity of the peroxidizing body.

necessarily null on account of its complete lack of novelty.

GRAWITZ'S PATENT OCT. 21, 1876,

No. 115160.

FOR THE PRODUCTION IN DYEING AND PRINTING OF UNALTERABLE ANILINE BLACK.

The object of the present patent is :

1st. To specify the chemical nature of aniline black in a perfect, unalterable state ;

2d. To determine the conditions of its production.

3d. To reserve to myself the exclusive right for its direct production, or to subsequently change imperfect to perfect blacks.

The blacks in the perfect state present the double specific character, that they are not turned green by gaseous or liquid sulphurous acid, and that they do not dissolve in cold sulphuric acid of 66° Bé., which only holds them in suspension, so that they are deposited, on the addition of water, as a black powder.

The imperfect blacks, the only kind given by Lightfoot's process, become green with sulphurous acid, and dissolve in sulphuric acid, allowing their deposition, on the addition of water, as a green powder.

My blacks are developed altogether without exposure to air, by the action of chromic acid in solution, or by acid chlorates.

The production of a perfect black, requires that the chromic acid exercise its action at about 80° C., and the same is effected in the case of chlorates by steaming.

The conduct of the operation of heating with chromic acid is delicate.

REMARKS ON GRAWITZ'S PATENT OF OCTOBER 21, 1876,

No. 115160.

The history of the actual discovery of Grawitz is at once amusing and characteristic on account of the painstaking manner of that inventor. We take the following on the authority of Camille Kœchlin.[1] "In response to your request for evidence, I can not do better than give the history of our relations with Samuel Grawitz. Grawitz was recommended to us by a near relation; we received him in consequence as a friend, and placed our laboratory at his disposal. He took advantage of this without hesitation, and during many months experimented in working out his ideas in regard to dyeing black. He worked....." (we replace the words of Kœchlin with the softer expression *very slovenlily*) for most of the time without weights or measures.

"In October, 1876, Grawitz, believing his process to be sufficiently studied, proposed it to various houses, among others to a bleacher and dyer in our vicinity, H. Hœffely & Co. As the black dye of Grawitz appeared to have some value in the eyes of Hœffly & Co., it was necessary that it should not green. The black of Grawitz did green. Grawitz requested authority from us to add to his process our method of rendering blacks ungreenable. That authorization was accorded him; our receipt

[1] Extract from a letter from Camille Kœchlin to Wilbaux Florin, of Dec. 23, 1877.

GRAWITZ'S PATENT NO. 115160 OF OCTOBER 21st 1876.

It is better to operate as follows:

In dyeing cold or lukewarm, to 100 parts aniline, 160 to 180 parts acid bichromate is use. The black thus obtained is imperfect. To change the imperfect into perfect blacks, treat the textile materials, after rinsing, with the following reagents:

No. 1	Copperas	20 kilos
	Bichromate	6 "
	66° Sulphuric Acid	16 "
	Water	60 "
No. 2	Bichromate	3 kilos
	Water	10 litres
	66° Suphuric Acid,	2½ "

5 litres of reagent No. 1, or 2 litres of reagent No. 2, may betaken to 800 litres of water. Heat to above 80° C. and work in it three-quarters of an hour, adding a little of the reagent if necessary.

The chlorates, which exert an action of the same kind on steaming, are the chlorates of aniline and alumina. The black always greens a little with chlorates.

Nitrous acid, sulpho-nitric acid and acid oxidizing agents in general, have the same action.

The same reagents transform into perfect blacks the imperfect blacks, which are the only ones given by Lightfoot's process, employed in printing.

The black in the perfect state may have three reflexes, maroon, true black, of blue-black.

By abridgment the process gives unalterable grey.

These bodies, the perfect black, the unalterable grey, having a definite chemical existence, which I have first produced on fabrics, I reserve to myself the application

was given to him, but with the condition *that it should not be used in the works of Hœffely & Co., who were not friendly* as regards business affairs with us. Grawitz, took our process, and commenced with Messrs. Hœffely as parties to the black, leasing the process to them instead of making it, but this giving no signs of life, he proceeded to offer our process for rendering blacks ungreenable to our competitors, Gross, Roman, and Marozeau of Wesserling. He there presented himself IN OUR NAME, and made a good bargain, probably to the amount of 3,000 to 4,000 francs, did not show himself again at Mulhouse, but made a circuitous route to avoid it, to take the train for Paris the same night. At Paris, he legalized his trick, by patenting our process for himself."

We do not see how this very ingenious and eminently practicable process of Jeanmaire, (a chemist retained at that time by the firm of Kœchlin Bros.), should constitute a patentable invention for the author, after the patents and publications of Lauth (pp. 65 and 66.)

The same agents, per-salts of iron, chromic acid, etc., are there pointed out, as well as heating. The merit of Jeanmaire is not diminished, as he was ignorant at that time of Lauth's process.

It is fortunate, that colorists having so much skill, held these secrets for a longer or shorter time, subsequently allowing them to become public property, but never dreaming of claiming a monopoly of them.

The pretense of Grawitz to reserve to himself the ungreenable black is absolutely ridiculous.

The ungreenable black existed long before the patents of Grawitz (se Cordillot, Lauth, Glanzmann and others); and he found in *publications* anterior to his patent a multitude of reactions, which judiciously employed furnished him the patent.

of, in dyeing and printing, although it may be found to be modified in practice.

Such is the *ensemble* of reactions, processes, and applications, which I claim by the present patent.

The experts of Douai place themselves on this side (see p. 134 to their report), by saying: that he did not base his patent of *new processes* for the preparation of that color. Now, the procesess of Grawitz contain absolutely nothing new.

On comparing the patent of Grawitz with the sealed statement of Kœchlin Bros., their almost complete identity is seen.

Grawitzs has, however, for a long time denied the indelicacy which he committed. See what he has written to the editor of the *Moniteur de la Teinture*, April 28, 1879, (p. 101 of that journal):

Jeanmaire freely placed his formula at my disposal, about October, 15, 1876, but neither he, nor any other person, has the right to use it without my authorization for it falls within the scope of my patent of 1874. Some time after, I learned that an indiscretion had placed persons strangers to the house of Kœchlin Bros., in possession of that formula. I then patented it, comformably to the text furnished me by Jeanmaire, to paralyse the aggressions of those persons."

These lines are *simply exquisite, such imperturbable sang froid astonishes us even on the part of Grawitz.* He knows well enough to tell us, how the processes of the Messrs. Koechlin fell within the scope of his patents of 1874; but we see no account of it there, all that we see in these patents in question, is that they themselves fall within the scope of previous patents.

But aside from all other considerations, the present patent shows, that in October, 1876, Grawitz *only knew how to make imperfect, that is to say, greening blacks.* If the processes of his previous patents gave, under certain conditions, *perfect, non-greening blacks, the inventor did not know it himself.*

REMARKS ON GRAWITZ'S PATENT NO. 115160.

Note again, that the process for rendering blacks non-greening, had been discovered by Camille Koechlin. Durand and Huguenin, the introducers in this industry by rendering commercial, of sulpho-nitric acid, (a solution of nitrous in sulphuric acid), for fixing blacks.

CERTIFICAT D'ADDITION OF MARCH 22, 1877,

ATTACHED TO PATENT NO. 105554.

I announced in my last *certificat d'addition* to my patent of Nov. 3, 1874, the delicacy of dying with heat with chromic acid and chromate of aniline.

In order to guard againsts these accidents in dyeing, it may be conducted as follows :

The bath being made up with a salt of aniline and bichromate of potash, acidified by an acid in the proportions indicated, conduct the operation entirely in the cold for from one-half to three-quarters of an hour. The temperature may then be raised even to boiling if desired, and kept at 100° C. for about one-half hour.

The heating may be done by a fire or with steam.

The blacks obtained in this manner, as well as by the process already described, in the patents I have taken, that is to say : mordanting in baths containing a salt of aniline and a per-salt of iron, for example, then oxidation in acid bichromate, and that by successive dips in the cold ; or as well, by mordanting with the aniline salt of a metallic acid, for example, in acid chromate of aniline, then fixing with heat by a passage through a hot per-salt of iron ; the blacks, I say, found in these three manners, or by mixed processes derived from their combination, are insoluble in sulphuric acid, and do not green in the air, nor even under the action of sulphurous acid.

There may also be obtained, by diminishing the proportion of aniline per kilo. of textile material, a series of grey shades more or less deep, by the same processes.

REMARKS ON THE CERTIFICAT D'ADDITION

OF MARCH 22, 1877.

No more than the first *certificat d'addition* has this anything to do with the principal patent. (See our discussion of the first *certificat d'addition.*)

Grawitz is found under this heading, maintaining a veritable practical process for dyeing non-greening aniline black.

See how they came by it:

1st. Bobœuf, Paraf-Javal, and Persoz, had indicated the dyeing in a single bath with bichromate, salt of aniline, and acids,

2d. Persoz had shown that a mixture of sulphuric and hydrochloric acids well agitated is better than either of the two acids separately, Jeannolle had also employed the two acids.

3d. The employment of heat to render the black fast, had been indicated in a series of patents and publications.

Grawitz had not however understood its importance, until the process of the brothers Koechlin had been communicated to him.

The sealed paper of the brothers Koechlin had been opened Nov. 29, 1876.

Every one in the industry had, in processes which were public property, means of rendering blacks non-greening; this sufficed to open his eyes. Grawitz, as well as others had the right to furnish himself from a common source; but what we contest with him, is the right to make a monopoly for himself from what belonged to all the world.

We are convinced that the courts will be our opinion.

CERTIFICAT D'ADDITION TO PATENT NO. 105554 OF MARCH 22, 1877.

Example of dyeing a grey for 10 kilos. cotton :

Water.....	200 litres.
Aniline.	250 cc.
Muriatic Acid of 22° Bé....	250 cc.
Bichromate of Potash.....	550 grams.
Sulphuric Acid 66° Bé.....	250 cc.

The presence of other metallic salts than salts of chromium in the dye-bath allows a variation of the shades of grey more readily than those of the blacks.

These non-greening blacks, these non-greening greys, I have first produced and patented as new bodies independent of any process for their production.

The bronze maroon-black obtained by dyeing in the cold with chromic acid is very salable and suffices for many articles.

Blacks may also be fixed by dyeing in the cold and then lukewarm, in a bath containing chlorate of potash, a salt of aniline and per-salt of iron, for example, then pass at boiling or near 100°C., through a dilute bath of chromic acid, containing also sulphuric acid to hold the oxide of chromium in solution.

Non reducing acids also transform at 100°C. into fast blacks, the bronze-blacks obtained by dyeing in the cold with chromic acid.

Such is the *ensemble* of processes, products and applications which I intend to reserve to myself by the present *certificat d'addition*.

We give in conclusion, two more patents and a *certificat d'addition* of Grawitz, although they have no practical value, and so far as we know, there is no question in this respect as to all his patents.

PATENT NO. 105555 OF NOV. 3, 1874

FOR THE PRODUCTION OF A SERIES OF COLORS FROM ANILINE AND OTHER BASES, SUCH AS TOLUIDINE, ROSANILINE MORE OR LESS SUBSTITUTED, NAPHTYLAMINE, ETC.

"The method which I intend to reserve to myself for the production of a series of colors in dyeing and printing is based on this fact: substitution in aniline or other bases for one or many molecules of hydrogen, of one or many molecules of a metal, whatsoever it be, then oxidation of the complex base resulting therefrom, by chromates or bichromates, or also soluble chlorates, in liquors neutral or even acid, by chlorides and hypochlorites, by steaming or by exposure to air, oxidizing at above ordinary temperatures.

"In place of forming the complex base, I reserve myself the putting together of the metallic and basic elements, the two being in the state of salts. In the same manner, the elements of a double salt may be put together, fixed by dyeing or printing, and then oxidized by the means already stated.

"The metallic molecule, taking the place of a molecule of hydrogen, gives a very great stability to the subsequent products of oxidation, on account of the stability of metallic oxides and the affinity of metals for oxygen.

"My complex bases are comparable to ammoniide of

copper. These will be anilide of copper, rosanilide of copper, naphtylamide of copper, of iron, etc.

"My complex salts may be compared to double ammoniacal salts.

"I reserve to myself all the bases and all the metals, to submit them to this special reaction.

"When iron is employed, it is more convenient to employ the ferrocyanide or ferricyanide of the base under consideration.

"As these salts or their bases require further oxidation, it is evident that the metallic salts at their highest degree of oxidation should be employed.

"Such is the *ensemble* of processes and application of which I reserve myself the employment in dyeing and printing."

If the patents of Grawitz for dyeing and printing afford a measure of his practical capacity, this patent throws a flood of light on his value as a theoretical chemist. We recommend its study to our fellow-chemists.

One may be spared the detailed examination of experiments which have never been made, but only "reserved."

The pretence of reserving all the metals and all the bases to submit them to this special reaction is very original. Why has not Grawitz reserved to himself for five years all the reactions of organic and mineral chemistry.

PATENT NO. 124581 OF MAY 18, 1878.

"The invention consists in replacing the salts of iron or copper, which figure in the first recipe for the production of aniline black in presence of chloric acid given by John Lighfoot, by chromic acid or its compounds. The salts of vanadium have already been indicated for the same purpose. The minute proportion of vanadium necessary to produce the black has also been pointed out.

"Chromic acids and its salts act with an energy, at least, as great. The low price of these compounds admits of their economical employment in larger quantities than vanadium compounds, the generation of the black taking place either very slowly or very promptly, according to the proportions employed. The color is developed either by exposure or by steaming, or by the two actions combined. The chromic reagent is either made up in a paste with starch or otherwise, or placed in advance on the fabric.

By applying either on one side or both sides, a uniform color is obtained.

"In conclusion, the improvement which is made the object of the present patent consists in replacing the salts of vanadium, in all their applications to the production of black from aniline in presence of chloric acid, by chromic acid and its compounds.

"P. S.—The salts of sesquioxide of chromium also engender the black, but their action is less energetic; I also claim their employment."

CERTIFICAT D'ADDITION OF MAY 7, 1879,

ATTACHED TO PATENT No. 124581.

"The metallic agent, which, in the generation of aniline black, determines the decomposition of the chlorates, was formerly a compound of a metallic oxide and hydrosulphuric or hydrochloric acid.

"By my patent 124581, I demonstrated that peroxide of chromium (chromic acid), or the combination of this peroxide with oxides (chromates), in general determine the generation of black, with this great advantage, that the liquors become more basic as the reaction proceeds.

"Oxides of a degree of oxidation higher than the first of the following metals act in the same manner: iron, manganese, copper, nickel, cobalt.

"The object of the present certificate is to reserve to myself their employment, and also that of their combinations with carbonic, oxalic, tartaric and acetic acids.

"The mechanism of the reaction is the following: the acid combines first with the aniline, becoming free as the aniline is transformed into black.

"This acid saturates itself with the metallic oxides employed, or their combinations with weak acids.

"In this way the weakening of the tissues is obviated, even when the reaction takes place at a high temperature, 70°–80°C. for example.

"With the salts of iron non-greening black is obtained, as I have already announced, as also with the oxides of iron.

"Such is the *ensemble* of processes, or products, and of reactions, which I intend to reserve to myself by the present certificate."

"I apply this *ensemble* of processes to pure or commercial aniline, to its homologous bases, to naphtylamine, and other amines."

Grawitz addressed at the same time that he took out his patents a note to the Société industrielle de Rouen, from which we extract the following passages:

"*Chromic acid and its salts exert in mixtures for black a much more considerable energy than the salts of vanadium.*

"*In mixtures not thickened, or thickened slightly with gum arabic, the black is also developed by adding one-tenth of a milligram of bichromate of potash to a litre of color containing 100 grams aniline in the state of a salt.*"

The société industrielle de Rouen charged three of its members, Lamy, Glanzmann and Witz, to experimenl on this patent. These gentlemen, as stated by their reporter, Witz,[1] *obtained absolutely negative results, and Grawitz has never succeeded in invalidating the conclusions, with which he is overwhelmed, of these skillful practical chemists.*

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[1] *Bulletin de la Société industrielle* 1878, pp. 579-585.

OPINIONS OF VARIOUS SCIENTISTS ON THE VALUE OF GRAWITZ PATENTS.

The patents of Grawitz have already given rise to a great number of discussions and reports.

Grawitz having commenced, in 1877, a suit against Wibaux-Florin and Gaydet père et fils, before the tribunal of Lille, the expert examination was confided to Ch. Violette, B. Corenwinder, and J. Lacombe.[1]

These gentlemen drew from the study of anterior publications and their personal experiments the following conclusions :

"1st. The processes found described in the patents and certificats d'addition of Grawitz, having for their object the dyeing with aniline black, do not constitute a new invention.

"2d. They can not be considered as new applications of known methods, susceptible of giving industrial products as their result."

The authors in question, find, in effect, sufficient to annul the patents of Grawitz, in priority of the patents of Perkin, Lightfoot, Bobœuf, Jarosson, and Mueller-Pack, and Jules Perzoz, and in fact that prior to 1874, aniline black was commonly dyed in many works.

[1] Rouen, printed by Léon Brière, 1880.

In consequence of this report, the tribunal of Lille annulled the Grawitz patents, but this order was amended by the Court of Appeals at Douai, and an new expert examination confided to DeLuynes, Friedel and Jungfleisch?[1]

Messrs. Wilbaux-Florin and Gaydet père et fils, entered[2] with the court at Douai a "Mémoire de refutatation," very voluminous and extremely remarkable from the abundance of sources drawn on the discussion of the pretensions of Grawitz.

This memoir of refutation, is in our opinion, a most interesting work. The bibliography of aniline black up to 1879 is there reviewed in an extremely complete manner, and the pretensions of Grawitz are thus reduced to their just value.

To us it appears almost incredible that, in the presence of these documents, the suit had not ended in the complete defeat of Grawitz.

Supported by arguments which seem to us irrefutable, Wibaux and Gaydet claimed the annulment of the patents.

De Luynes, Friedel and Jungfleisch, the experts commissioned by the Court of Douai, arrived at entirely opposite conclusions, basing themselves on anterior publications, as well as experiments made by themselves alone, or in common with other parties.

According to them, "The processes found described in the patents and *certificats d'addition* of Grawitz, and which lead to the direct obtaining of non-greening aniline black, in dyeing or in printing, constitute *a new*

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[1] Paris, Renou et Maulde, printers and lithographers, 1885.

[2] Paris, printed by Tolmer & Co., 1882.

application of known methods, giving a result industrially novel.

"The processes, having for their object the fabrication of a non-greening aniline black in paste and in powder, and of transforming greening into non-greening blacks, constitute *new methods of obtaining a result industrially known.*

The experts stated "that fabrics had been printed and dyed in aniline black *before the Grawitz patent*, and that such oxidizing agents as the salts of copper, alkaline chlorates, bichromate of potash, acids, etc., had been employed in such dyeing *before the Grawitz patents* (p. 61 of the Douai report).

They established also that the non-greening black was known before Sept. 30, 1874, and was public property (p. 134 of Douai report), and that in order to obtain a patent he must base it on *new processes* (p. 136, *ibid.*).

In effect, the blacks in powder of Perkin and Glanzmann are non-greening. The experts thought that these powders had remained without usage. We have shown (p. 19) that this is not so. On the contrary, the blacks in powder, prepared according to many different processes, had been used industrially from 1862.

The experts admitted "that there had been described, particularly by Lauth, processes for transforming greening into non-greening blacks, but there had been no public process permitting direct dyeing in a single bath, or to print at one operation a non-greening aniline black" (see p. 135 of Douai report).

We will remark, that the black of Lauth is ungreenable by itself, if operated by dyeing with heat, that the blacks of Cordillot become non-greening by steaming—this was universally practiced in 1874—(p. 51), and that

the blacks of Bobœuf, Paraf-Javal, Persoz, and many others, *dyed with the aid of heat*, are equally so.

On examining authorities, the experts of Douai could see nothing of a character to invalidate the patents of Grawitz.

On this account *we absolutely dissent from their opinion.* It seems to us, that, on examining the documents we have published on the preceding pages, *documents of which a portion was unknown to the experts*, the conviction has not been taken away, *that all that is found in the Grawitz patents, with the exception of some absurdities and errors, was known previously*, and that these patents are, in consequence, valueless; we will revert to this again under our "Conclusions."

The finding of the experts of Douai has occasioned a painful surprise, not only in France, but also in foreign countries, although in other countries the Grawitz patents are worthless (see note to p. 161).

In the *Chemiker Zeitung* of Coethen (1886, Nos. 54, 60, 74, 80 and 88), a Swiss colorist, Henri Schmid, discussed the Grawitz patents thoroughly. His articles all have a special interest, in view of the recognized authority of the author in all relating to dyeing or printing, and his absolutely disinterested position in the question.

It is a masterly demolition of the pretensions of Grawitz. In a "technical consultation of the dyers of France on the value of the patents of Grawitz," Chas. Girard, L. Magnier de la Source and J. Ogier[1] alike expressed a belief in their entire nullity. They established positively that these patents lacked novelty, and that, aside from the first two, No. 105130, of Sept. 30, 1874, and No. 105554, of Nov. 3, 1874, they were defective on account of the *insufficiency of description.*

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[1] Rouen, printed by Leon Brière, 1887.

They finally showed that he followed the directions of Bobœuf's patent for obtaining a practically ungreenable black in a single bath.[1]

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[1] To the conclusions of this report A. W. Hoffman, the savant so justly celebrated for the number of his researches on coloring matters, Professor in the University of Berlin, and correspondent of the Institute of France; Graebe, the inventor of artificial alizarin, Professor in the University of Geneva; O. N. Witt, Assistant Professor at the Polytechnic School at Berlin, well known for his important researches on artificial coloring matters; and Nœlting, Director of the School of Chemistry at Mulhouse, have all assented.

A. W. Hoffmann expresses himself as follows:

"The undersigned, consulted by the dyers of France in regard to the value of the different patents taken out by Grawitz for the production of aniline black, declares as follows:

"Having been member of the Imperial Commission of Patents (*Kaiserliches Patent-Amt*) from its commencement in 1877 to the year 1882, I can affirm that Samuel Grawitz, chemist, of Paris, demanded, under date of Dec. 8, 1877, before the Commission of Patents, the change of his patent, taken Apr. 10, 1875, for Alsace Lorraine, as well as his *certificat d'addition*, dated Feb. 26, 1877, into a patent for the German Empire, and that the demand was refused in both instances.

"This refusal was due to the lack of novelty of the processes described in these documents.

"See in the following prior publications what was known prior to the patents of Grawitz:

"*Wagner's Jahresberichte*, the first 15 volumes, in particular vol. for 1865, p. 619, vol. for 1871, p. 775, and vol. for 1872, p. 711,

"*Schützenberger-Schrœder, Farbstoffe*, Berlin, 1868, Vol. I, p. 508.

"A judicial demand addressed at the mediation of the French ambassador to the Commission of Patents, at Berlin, did not fail to bring official confirmation to the facts announced in my declaration.

"Berlin, Apr. 29, 1887.

"A. W. HOFFMANN."

(Signature certified to.)

CONCLUSIONS.

It will be permissible in conclusion to resume our examination of the contents of Grawitz's patents, and discuss their aggregate value.

The author, in 1874, who at that time *appears ignorant of the most elementary principles of dyeing and printing*, found in the publications of Schiff and of Higgin the word *metal-aniline*. The word was to his taste, he seized it, and evolved from it a theory of *metal-aniline black*, "my black." This is in his first patent of Sept. 30, 1874; he produced not really copper-aniline, or anilide of copper, *which has no existence*, but the salts of phenyl-cupramonium. He wished to oxidize them by chromates or chlorates. But, alas, the reaction did not take place; it only occurred with salts of aniline, or, better still, with an excess of acid. So, abandoning his patent after three days, he perfected it by taking processes employed by all the world. He speaks always of *metal-anile*, it is true, but, in reality, he does not have it. The salts of copper-aniline are only formed by *free aniline* and the salts of copper; with the salts of aniline in some cases, double salts are formed, in others only a simple mixture results. The double salts of aniline and copper had been employed long before Grawitz by Lightfoot among others (hydrochloride of aniline and chloride of copper).

Doubtless perceiving himself, that his patent, No. 105130, of Sept. 30, and the *certificat d'addition* of Oct. 20, 1874, contained nothing new except errors and

some impracticable processes for printing, that they were worthless and their annulment would soon be demanded, Grawitz took out, on Nov. 3, 1874, a second patent, No. 105554, especially for dyeing. Here he asked nothing less *than to reserve to himself the exclusive right during five years of dyeing fibres of all natures.* Grawitz has doubtless himself felt the ridiculousness of such pretensions. If he alone had the right to dye aniline black, why has he taken out later patents?

The black is yet a black of metal-aniline, but only "very probably;" it is formed in two stages, first by the oxidation of a salt of aniline by a per-salt of iron or copper, then peroxidation by acidified bichromate, which is as old as the world.

In a second *certificat d'addition* to the first patent, No. 105130, Grawitz recapitulates, on April 29, 1875, his processes based on the "concomitant action," and claims the employment of a great number of metals.

The processes for printing are either not new or are impracticable, while the process for dyeing in two baths resulted from the combination of the processes of Kopp and Wood and Wright. This is ancient history. The author here insists particularly on the necessity of employing acid baths, while at first he had claimed, as an improvement, the employment of basic aniline salts.

In all these patents and *certificats of addition* it is always the question of dyeing in two baths or by alternate passages; the employment of heat is not mentioned. Notwithstanding, in *previous publications*, the fact had been noted that *the blacks dyed with heat were faster.* We shall see that Grawitz more slowly claimed for himself the employment of heat, that physical agent, of which the dyers availed themselves daily, without believing that is made a patentable discovery.

The patents of Grawitz up to this time do not appear to have had the success the author anticipated. In 1875

and 1876, many patents (Coquillion, Jeannolle) and publications (Gouillon), had appeared, touching the perfecting of dyeing with aniline; so that Grawitz felt himself compelled to take out, August 24, 1876, a new *certificat d'addition*, this time to his second patent, No. 105554, in which, under pretext of recapitulation (an extremely convenient pretext), annexed to himself these new improvements.

Here we have, for the first time, the single bath, the plain bath, containing all the elements for the production of the black. Not daring to claim it at once, he commences to speak of dyeing in three baths, like Jarosson and Mueller-Pack, then of dyeing in two baths like all the world, in particular Bobœuf, Alland, Persoz, &c., so as to finally arrive at dyeing in one bath, like Bobœuf, Paraf-Javal, Tantin and Brière, Persoz, Pinckney and Jeannolle. It always appears as metal-aniline —at least such is Grawitz's intention, that is to say, in reality, a double salt of aniline and copper, but the chemical equivalents are thrown overboard: for 6 kilos aniline, he took only 250 grains bichloride of copper, instead of the 4.323 kilos of anhydrous *Cu Cl*, demanded by equivalent formulæ; and, to complete the sentence, he adds: *the copper may be omitted.* Then what becomes of the metal-aniline? Grawitz was doubtless convinced of his inanity, and that he was following in the steps, more simple it is true, of the patents of Bobœuf, Paraf-Javal and Persoz.

It was surely unnecessary to use so much circumlocution to arrive at where another had been eleven years before.

Nevertheless, these are always "his blacks," and the *ensemble* of reactions—increased by worthless ones of his own invention, and which were known long before —become "his property." It must be owned that Grawitz is not lacking in dissimulation.

Note again, that dyeing with heat and chromates is still, in the eyes of Grawitz, "delicate, and it is thought better to proceed in the cold." He did not apprehend, until somewhat later, that the brothers Kœchlin had judiciously employed heat.

The patent of October 21, 1876, is, so to say, the literal reproduction of the sealed paper of the brothers Kœchlin (p. 75). This sealed paper contained very ingenious methods, but does not seem patentable to us, for they are contained by implication in the patents and publications of Chas. Lauth.

The inventors have judged thus, or doubtless they would have patented their process themselves.

Therefore, if Grawitz, instead of *appropriating* the process in question, had discovered it himself, it would not have made it a valuable patent.

The *certificat d'addition* to the second patent, No. 105554, of March 22, 1877, gave some excellent and industrially applicable processes, but after anterior publications, it contained nothing new.

The pretensions of Grawitz have differed according to the time; modifying his claims as far as they were opposed by his predecessors; claiming in accordance with their discoveries:

1st. For blacks in powder.

2d. For blacks in printing.

3d. For black in dyeing in one, two or three baths.

4th. For the transformation of greening into non-greening blacks.

5th. For the direct production of non-greening blacks at a single dip.

All these claims are, after what we have established in this study, as little justified one as another, and the *total abrogation of all the Grawitz patents* is imposed, in our opinion, in the most absolute manner.

In the conclusion presented May 7, 1876, before the tribunal of Laval, Grawitz, pushed to his last intrenchments, declared *that he claimed neither the principle of the production of aniline black, nor the exclusive right of dyeing all materials with aniline black; nor in general, the exclusive employment of all methods whatsoever for rendering a black non-greening, and that he limited his claims* TO HIS MANNER OF PRODUCING AND DYEING ANILINE BLACK.

This retreat appears to do great honor to the talents of Grawitz as a tactician. His pretentions have now so modest an air; he no longer claims the property to aniline black in general, but only to *his own means of producing it.*

Who can have so hard a heart as to refuse him that? But look out for the trap! *The means of producing the black of Grawitz are evidently found in his patents*, BUT IN THESE PATENTS HE ENGROSSES ALL THAT HAD BEEN DONE BEFORE HIM, AND IN GENERAL, ALL THE POSSIBLE PROCESSES FOR THE PRODUCTION OF BLACK. All this has an air of restricting his pretensions. Grawitz has not laid stress on it, but if his demands were accorded, no other person could make aniline black.

Specifying his claims in regard to dyeing, Grawitz claims for himself the process of the "PLAIN BATH." This process consists *in placing together in the same bath the elements producing aniline black and the fibre to be dyed, plunging this into the mixture and allowing it to saturate itself, becoming charged with color, in such a way that the fibre becomes dyed with the black, which is produced insoluble, all of the materials being in solution;* he claims as his property the process of dyeing in a plain bath, continued until the black becomes ungreenable, or it may be arrested on the way, before the moment is reached when the black becomes chemically ungreenable. *It is the fact of placing the*

fibre in a bath containing a mixture of the producing elements of the black, and leaving it there until the color to be dyed is produced on the fibre, which constitutes the process which he claims.

That is to say, in other words, that Grawitz claims all the possible processes of dyeing in aniline black. This is his old claim, "*the exclusive right of dyeing in aniline black fibres of all kinds*," under a different form.

We will first remark, that Grawitz interprets incorrectly the phenomena which take place in the deying in a plain bath. It is not with the insoluble aniline black that the fibre dyes itself, as if this color was soluble. The fibre in the plain bath contains, for example, salt of aniline, the chromic acid and acid absorb those substances which are soluble, and the insoluble black is only formed in the fibre.

The mode of the formation of black that Grawitz claims for himself, does not belong to him in any way, the greater part of his predecessors had not operated otherwise.

First, the plain bath, containing all the elements for the production of the black, and in which the fibre is plunged, as found indicated by Bobœuf, Paraf-Javal, Persoz, Tantin and Brière, Coquillion, Pickney and Jeannolle; then the processes *for many baths* are engrossed by the claims of Grawitz. If, for example, we plunge, according to the processes of Bobœuf, the fibre in a bath of bichromate of aniline, then rinse the fibre charged with the salt in acidified water, the plain bath as defined by Grawitz is realized; there being in effect in the same bath, the fibre and all the elements necessary to the production of the black.

The claim of Grawitz of the plain bath for himself is an audacious attempt at industrial monopolization which the tribunals refuse to sanction.

From what we have developed it might be believed that we contest all merits on the part of Grawitz. Not so. We render full justice to his talent. He has arrived at the last of the many pleiades sought in the domain of aniline black, he has the skill to invade the ideas and processes of his predecessors, and by removing their marks to make them pass for his own; every time that improvements have been realized by others, he has under pretext of recapitulation, claimed them for himself. He has invented nothing new himself, but has passed himself off as the father of dyeing in aniline black; by his pseudo-scientific lucubrations, he has known how to throw dust in the eyes of those who might be supposed to have more perspicacity, and in such good order as to succeed each time; he finishes by making for himself a monopoly abusive and detrimental to a French industry, while in foreign countries the discoveries are used freely (see the note at foot of p. 157), by which numerous modest and disinterested workers have enriched science and industry.

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Made Without Pressure.
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Not Liable to Sour.
Has all the Advantages of Ground Sumac with None of its Inconveniences.

Such an article, it is conceded by the largest intelligent consumers in the country, was not known in this market up to the year 1886, when we undertook the manufacture of it. Up to that time the sellers of Sumac Extract simply sold it on its specific gravity, a custom which admitted of adulterating the extract with anything and everything, and which resulted in compelling the dyer for his own protection and safety, to boil out the ground sumac for himself.

Recognizing the necessity for a pure and reliable quality of Sumac Extract at a reasonable price, in 1886 we equipped a works on the water front on the New York Harbor, for the manufacture of Sumac Extract on a scale larger than had up to that time or has since been attempted. We claim that the gain to the consumer of Sumac Extract in the improved products that have been offered since that time, is due to the absolutely pure and stable article which we then began manufacturing and selling, and secondly, to the means of determining the relative merits of Sumac Extract, which we put into the hands of every consumer, by the publication of the "Standard Method for Testing Sumac Extract," revised and approved by Albert R. Ledoux, M. S., Ph. D., Henry Trimble, Ph. G., and P. de P. Ricketts, Em. Ph. D. We challenge any competitor to furnish an article in value and purity, superior to that made and sold by us.

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For sizing, finishing and polishing Cotton, Linen, Jute, Silk, Worsted and Woolen Yarns or Fabrics.)

MERITS. Absolutely Neutral, neither Acid nor Alkali in its composition.
Antiseptic, not liable to mildew.
Unaffected by extremes of heat and cold.
Will not affect the most delicate color.
Can hold in suspension a large amount of clay.
And increases that property in Starch, Flour, Farina, &c.
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Prevents dusting off by laying the fiber, giving a smooth thread.
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Put up in barrels of about 500 lbs. each. No charge for packages.

General Directions for using STAR SIZE.

FOR COTTON WARP SIZING OR DRESSING. Add to the ordinary quantities of Starch or other Sizing material employed, 25% to 50% of STAR SIZE previously dissolved in boiling water with brisk stirring, and boil up the whole for a few minutes.

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In 1883, when we took up the manufacture of Stannate of Soda, none of the dealers in this article, and few if any of the manufacturers of it, were willing to guarantee to the consumer, the percentage of soluble or available oxide of tin (S. n. o. 2.) it contained. In consequence of this, many of the larger consumers preferred to make it themselves, no matter what the cost, rather than risk using an irregular article, the strength of which no one was in a position to distinctly guarantee.

From the very start, we had analysis made of every lot before offering same for sale, and warranted every package sold to contain the percentage of soluble tin oxide claimed for it.

Our Stannate of Soda is manufactured by a patented process, enabling us to secure the tin used in the compound at no cost whatever, and allowing us to sell the Stannate of Soda at prices below the cost of the materials used by any any other process.

We guarantee every pound of Stannate of Soda we sell, to contain the percentage of soluble tin oxide claimed for it, and shall be glad to send any users of Stannate of Soda, a standard method for testing this product, prepared for us by Dr. P. de P. Ricketts and Dr. Ledoux, with which pamphlet you will be able, whenever you see fit, to verify the guarantee we give as to the strength of our Stannate of Soda.

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Our works for these products, which are located in 12th Street, South Brooklyn, were erected several years ago, for the purpose of making them on such a scale as would enable us to enter fully into competition with similar imported articles.

The plant employed is of the newest and most improved type, producing economically the above named articles. Our brands are now well known on the market, and for purity, strength and cheapness, they are unequalled.

While we make regularly a certain number of types which have found favor with the consumers, we wish to state distinctly we are always ready to match samples of any quality at the lowest possible price.

Knowing that the qualities of our products are of such a character that they could not be excelled, and that our prices are so low as to make us court comparison, quality being considered, with any other makes, whether imported or domestic, we published two years ago detailed methods for testing Indigo Extract, which publication we should be glad to send to anyone interested in the above named product.

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We have quite recently turned our attention to the production of this article, which is always in demand, and we expect that through care and constant attention to this branch of our business, in the near future, we shall be able to give as good an account of our workings in this particular branch as we are now able to do in our Sumac Extract and other manufactured products. We have the newest and most improved plant, and one of the best geographical locations. Our works being situated on the Harbor of New York, and having our own dock connected with the works, and with the rest of our property by rail, enables us to get our Logwood direct from the port of shipment without rehandling, or any expense for wharfage, etc.

We are in a position to furnish a Logwood Extract either solid or liquid, in its highest state of purity, down to any grade that may be called for.

Our Black Dyes for dyeing Cotton and Wool are equal to anything of the kind in the market, and we can give special inducements in prices on these articles.

We have also a solid Black Dye for Wool and for Cotton which dyes these products in one operation, without any accompanying mordant, and offer great advantages to people at a distance from Ports where Logwood arrives. We should be glad to furnish through any of our offices, samples of these products, and give quotations.

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